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Investigation of the Structural and Magnetic Phase Transitions in CeSi_x by Neutron Scattering

by

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A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology

July 1993

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Abstract

In an attempt to gain a greater understanding of the magnetic interactions within the rare-earth metallic alloy $\operatorname{CeSi}_x(1.60 \leq x \leq 2.00)$ and the validity of the various theories of magnetism, intermediate valency and the 'dense' Kondo effect that are commonly invoked to account for its magnetic behaviour, the structural and magnetic properties of $\operatorname{CeSi}_{1.80}$ and $\operatorname{CeSi}_{1.85}$ samples have been investigated using the technique of thermal neutron scattering. Spin polarized neutrons and neutron spin polarization analysis have been employed to unambiguously separate the paramagnetic and antiferromagnetic scattering of CeSi_x samples from all other scattering contributions.

The CeSi_x system has been found to undergo a variety of structural and magnetic phase transitions both as a function of temperature and silicon concentration. The crystallographic instability of CeSi_x (1.80 $\leq x \leq 2.00$) samples with the ThSi₂-type structure has been observed. The importance of the phenomena of silicon vacancy ordering and a crystallograhic distortion in minimizing the free energy of the CeSi_x system has been both observed experimentally and discussed theoretically. Such phenomena account for the significance of the sample heat treatment and subsequent cooling process on the crystallograhic structure of CeSi_x ($x \approx 1.80$). From experimental observations, it is suggested that the occurrence of an orthorhombic distortion in CeSi_x ($x \leq 1.80$) samples is a necessary condition for the formation of a magnetically ordered ground state.

Discussions are presented that highlight the importance of the electronic configuration and bonding of the atoms within the silicon sublattice in determining the stability of the crystal structure of CeSi_x. These discussions indicate that the introduction of silicon vacancies causes a decrease in the conduction electron density of CeSi_x with decreasing x. Though speculative, such a proposition enables many of the observed features of the structural and magnetic phase diagrams of CeSi_x $(1.60 \le x \le 2.00)$ to be understood, such as the non-magnetic \rightarrow magnetic ground state phase transition in CeSi_x with decreasing x and the existence of antiferromagnetic correlations in a paramagnetic CeSi_{1.85} sample. It is proposed that the absence of a magnetically ordered ground state for CeSi_x $(1.80 \le x \le 2.00)$ samples with the ThSi₂-type structure is caused by frustration effects. In view of this work, it is argued that alternative mechanisms can account for the structural instability of CeSi_x (1.80 $\leq x \leq 2.00$) samples and the non-magnetic \rightarrow magnetic phase transition as a function of x that are independent of the intermediate valency of the cerium 4f electrons or the existence of a 'dense' Kondo effect in CeSi_x . The occurrence of structural phase transitions and distortions of the crystal lattice are clearly of importance in relation to the magnetic phase transitions in CeSi_x and must be investigated further in order to clarify the dominant mechanisms that determine the magnetic behaviour of CeSi_x .

Acknowledgements

I would like to express my deepest thanks to Dr. K.-U. Neumann for the friendship, guideance and encouragement that I have received throughout the whole of this thesis. It has been a great pleasure to work with you and I have thoroughly enjoyed the last three years.

I wish to thank the Institut Laue-Langevin for the opportunity to undertake this thesis and all the scientists and staff who have made this work possible and my stay in France so enjoyable. In particular, Dr. P.J. Brown and Prof. O. Schärpf for their supervision, help and patience.

A special thanks goes to Dr. D. Visser for his help in performing the diffraction experiments and also to Prof. K.R.A. Ziebeck. Your thoughts and suggestions have been greatly appreciated.

I am grateful to Dr. J.K. Cockcroft and Dr. A.N. Fitch for their advice and help with the powder diffraction refinement programs. I would also like to thank Dr. S.T. Bramwell, Dr. J. Pierre and Dr. B. Lambert-Andron for their encouragement and many useful discussions.^{*}

I am indebted to all the 'mob' in Grenoble for a lot of fun over the last three years and for putting up with such a 'grumpy grouch' during the final few months. Thankyou Also a special thanks to Chris and Muna for looking after me so often whilst in Loughborough.

Last but not least, to all my family and Guga Though I couldn't ask you to do this thesis for me, I've always known that wherever you were, you would always help me to 'pick them up' at the end. Thankyou for all your love and support. I would not have finished this without them.

* I would like to thank J. Bates and N.K. Zayer for their assistance with the SEM analysis and also Dr. R.K. Kremer and M. Babateen for performing the magnetization measurements.

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For mum and dad.

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Notation

Roman symbols

a, b, c	unit cell lattice vectors
Cu	specific heat capacity at constant volume
ĉ+	conduction electron creation operator
ĉ	conduction electron annihilation operator
d(G)	number of symmetry elements in the group G
$\mathcal{D}\Gamma_{\iota}$	ι^{th} irreducible corepresentation of the magnetic group $\mathcal M$
E_{λ_i}	initial energy of target
E_{λ_f}	target energy following a scattering event
ε_F	energy of the Fermi level
$f(\kappa)$	magnetic form-factor
ĝ	symmetry operation of the group G
g(arepsilon)	density of electronic energy levels at energy ε
gj	Landé splitting factor
G	Gibbs free energy
$ ilde{G}$	point group of the space group G
G_0	space group of the high symmetry phase surrounding the phase transition
G_1	space group of the lower symmetry phase surrounding the phase transition
\hat{J}_{\pm}	component of the total angular momentum operator \perp to the scattering vector
$\hat{\boldsymbol{J}}_{jd}$	total angular momentum operator of the ion j, d
k_F	wavevector at the Fermi surface
k_i	incident neutron wavevector
k_f	scattered neutron wavevector
l.	dimensionality of the irreducible representation Γ_{ι}
M	magnetization (magnetic moment per unit volume)
\mathcal{M}	magnetic space group
$\tilde{\mathcal{M}}$	magnetic point group of the space group ${\mathcal M}$
N	'total-probability' order-parameter
\hat{p}_{e}	momentum operator of an electron
p_{λ_i}	probability of the target being in the initial state λ_i

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Ρ	incident polarization of the neutron beam
P'	polarization of the scattered neutron beam
q	reciprocal lattice vector
q_m	magnetic propagation vector
Q	Fourier transform of the total magnetization $M(r)$
x_c	critical silicon concentration separating CeSi_x samples that are single phase
	and those for which a coexistence of two phases is observed
x_{cs}	critical silicon concentration defining the transition between CeSi_x samples
	with non-magnetic or magnetic ground states
Ŝe	spin angular momentum operator of an electron
$S(\kappa,\omega)$	scattering function
T _c	Curie temperature
T_{cs}	critical temperature at which a phase separation occurs in CeSi_x $(x > x_{cs})$
T_N	Néel temperature
\hat{V}_m	magnetic interaction potential operator
\hat{V}_n	nuclear interaction potential operator
v_0	volume of the crystallographic unit cell defined by $v_0 = a.(b imes c)$

Greek symbols

Γ	ι^{th} irreducible representation of the group G
Δ	'disorder' order-parameter
Ô	time-inversion operator
к	scattering vector defined by $\kappa{=}k_i{-}k_f$
λ_i	initial state of target before a scattering event
λ_f	final state of target following a scattering event
ν_i	spin state of incident neutron
ν_{f}	spin state of scattered neutron
ξ	nuclear spin
σ	scattering cross section
$\hat{\sigma}_n$	Pauli spin operator for the neutron

$\chi_\iota(\hat{g})$	character of the element \hat{g} within the irreducible representation Γ_{ι} of G
υ	'distortion' order-parameter
au	reciprocal lattice basis vector

Physical constants (S.I. units)

h	= $6.62608 \times 10^{-34} \text{ J s}$	Planck constant
ħ	$= h/2\pi$	
k_B	= $1.38066 \times 10^{-23} \text{ J K}^{-1}$	Boltzmann constant
m_e	$= 9.10939 \times 10^{-31} \text{ kg}$	rest mass of electron
m_n	$= 1.67493 \times 10^{-27} \text{ kg}$	rest mass of neutron
m_p	$= 1.67262 \times 10^{-27} \text{ kg}$	rest mass of proton
μ_B	$= e\hbar/2m_e$	Bohr magneton
	= $9.27402 \times 10^{-24} \text{ J T}^{-1}$	
μ_N	$= e\hbar/2m_p$	nuclear magneton
	= $5.05079 \times 10^{-24} \text{ J T}^{-1}$	
μ_0	$= 4\pi \times 10^{-7} \text{ H m}^{-1}$	permeability of free space
N_a	$= 6.02217 \times 10^{23} \text{ mol}^{-1}$	Avogadro's number
R	$= 8.41351 \text{ J K}^{-1} \text{ mol}^{-1}$	molar gas constant
r_0	$= \frac{\mu_0}{4\pi} \frac{e^2}{m_e}$	classical electron radius
	$= 2.81794 \times 10^{-15} m$	

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Chapter 1

Introduction

In recent years there has been considerable interest in the physical properties of the rare-earth metallic alloy CeSi_x (1.60 $\leq x \leq 2.00$), both from a fundamental and practical view-point. The earliest experiments were performed in the 1960's as part of an investigation of the crystallographic properties of rare-earth disilicides and their dimorphism as a function of temperature. Following the observation of low temperature superconductivity in LaSi₂ (Hardy & Hulm (1954), Satoh & Asada (1970)) and LaGe₂ (Matthias et al., 1958), Yashima et al., (1982a) have investigated CeSi₂ and CeGe₂ during a series of experiments investigating rare-earth intermetallic compounds with the ThSi₂-type crystal structure. Their observation of an enhancement of γ , the linear coefficient of the electronic specific-heat capacity, initiated significant interest in the Ce-Si system within the 1980's as a compound exhibiting intermediate valence behaviour. Furthermore, upon the observation of a non-magnetic \rightarrow magnetic phase transition within silicon deficient CeSi₂ with decreasing silicon content (Yashima & Satoh, 1982), considerable experimental and theoretical effort has been directed at $\operatorname{CeSi}_x(1.60 \leq x \leq 2.00)$ and attempts have been made to explain its physical behaviour via spin-fluctuation effects and a 'dense' Kondo model (Satoh et al. (1982), Yashima et al., (1982b) and (1982c)).

More recently a significant practical interest has occurred in rare-earth disilicides due to their technological applications within the semiconductor industry when formed epitaxially on silicon (Knapp & Picraux, 1986). Such silicides are unique in that they have the lowest known Schottky barrier heights ($\phi \approx 0.3 \rightarrow 0.4 \text{eV}$) on *n*-type Si and a potential application in infrared detectors, ohmic contacts and as low resistance interconnects. These applications have stimulated a reinvestigation of the crystallographic and magnetic properties of rare-earth silicides in order to understand the metallurgical interaction of rare-earth thin films with silicon (Houssay *et al.*, 1989).

The motivation behind this investigation of the structural and magnetic properties of the CeSi_x (1.60 $\leq x \leq 2.00$) system has been to gain a greater insight into the factors influencing the magnetic interactions within this system and thus the validity of the various theories of magnetism, intermediate valency and the 'dense' Kondo effect that are most commonly used to account for such properties. Despite the fact that rare-earth silicides have been worked upon for almost thirty years, there is still a large variety of physical phenomena occurring within these systems that are not as yet fully understood. The technique of neutron scattering has been employed for this investigation since it provides the only method by which the magnetic interactions within condensed matter systems may be probed. Furthermore, the use of spin polarized neutrons and neutron spin polarization analysis enables an unambiguous separation of the magnetic scattering from all other scattering contributions.

In the following chapters, first a background to the fundamental formulae required for the description of the neutron scattering cross sections is presented. Subsequently, the structural properities of CeSi_x samples are investigated using the techniques of neutron and X-ray synchrotron powder diffraction and scanning electron microscopy. The macroscopic magnetic behaviour of the CeSi_x samples is measured by performing magnetization measurements in a Squid magnetometer and finally the microscopic magnetism is probed via the technique of x - y - z neutron spin polarization analysis. Following the experimental investigations, discussions are presented which attempt to determine the important physical mechanisms responsible for the various structural and magnetic phase transitions within the CeSi_x system.

The aim of this introduction is to present a preliminary overview of the physical properties of $CeSi_x$, both crystallographic and magnetic, and provide the reader with the background information that, throughout the remainder of this thesis, is assumed



Figure 1.1: The binary phase diagram of the Ce-Si system, courtesy of Moffat (1986). The horizontal arrows below the diagram indicate the region of the phase diagram that is being discussed within this work.

known. The portion of the Ce-Si phase diagram that is being discussed within the following chapters is illustrated in Fig. 1.1.

1.1 Crystal structure of $CeSi_x$

The intermetallic compound $\operatorname{CeSi}_x (1.60 \le x \le 2.00)$ exists in one of two types of crystallographic structure depending upon the concentration of silicon, x. The $ThSi_2$ -type structure is formed in the concentration range ($\approx 1.80 \le x \le 2.00$) and the $GdSi_2$ -type structure for smaller x. Fig. 1.2 illustrates the tetragonal ThSi_2-type crystallographic structure of CeSi_2. All silicon lattice sites are equivalent within this structure and the silicon atoms form a very open 'three-dimensional graphite' sublattice where each silicon is 3-coordinated with a bond angle very close to 120°.



Figure 1.2: The ThSi₂-type crystal structure of CeSi₂; a) cerium sublattice, b) silicon sublattice and c) CeSi₂.



Figure 1.3: The AlB₂-type crystal structure. a) Vertical projection; the shaded atoms are those that are translated in the transformation from the AlB₂-type to the ThSi₂-type structure. b) Side view; the shading is used to illustrate the plane of boron atoms.

The GdSi₂-type structure may be visualized by Fig. 1.2 but with a small orthorhombic distortion of the *a*-axis. There are two inequivalent types of silicon lattice sites within this structure. Out of the 74 intermetallic phases that are known to exist in either the ThSi₂-type or GdSi₂-type structure, all are either silicides or germanides with the exceptions of ThGa₂ and B₁₃Ir₁₂ (Villars & Calvert, 1985). It is thus believed that the silicon/germanium sublattice is of importance in determining the structural stability of these phases.

Dimorphism of rare-earth silicides $(RESi_x)$

Extending the discussion of crystal structure to the whole series of rare-earth compounds with the general formula $RESi_x$, there are three types of crystallographic structure by which these compounds are described; the ThSi2-type and GdSi2-type structures as described above and the hexagonal AlB₂-type structure. The latter is illustrated in Fig. 1.3. This structure is similar to the crystal structure of graphite except for the introduction of the rare-earth ions between successive planes of silicon. All three types of structure may be described as different arrangements of plates made with the same building element; a parallelepipedic polyhedron with eight silicon atoms at the apexes and a rare-earth atom at the center (Houssay et al., 1989). Such plates are stacked along the [001] direction in the tetragonal and orthorhombic structures, and along the [1010] direction in the hexagonal structure. The hexagonal structure is different from the former structure in the stacking sequence of the plates; successive plates are systematically translated by $\frac{a}{2}$ in the hexagonal structure while they are alternatively translated by $\frac{a}{2}$ or $\frac{b}{2}$ in the tetragonal and orthorhombic structures. The AlB₂-type structure may be transformed to the ThSi₂-type by a translation of the shaded atoms in Fig. 1.3a through a distance $\frac{a}{\sqrt{2}}$ along [2111] (Sekizawa & Yasukōchi, 1966).

For many years it was believed that all rare-earth disilicides were stable phases that exhibited a dimorphism (i.e. a stable existence in two different crystallographic structures) as a function of temperature (Perri *et al.* (1959), Mayer *et al.* (1967)). A summary of the results of the latter authors is given in Table 1.1 where the *amalgamate method* refers to samples prepared by melting the raw elements together at 450°C

Table 1.1:	Dimorphism	of rare-earth	disilicides,	Mayer	et al.	(1967), listed	for decreasin	ιg
size of rare	-earth ionic ra	adius.					· •	

Disilicide	Crystal structure for	Crystal structure after
of	'amalgamate method'	heating up to 1600°C
Ce	Tetragonal	Tetragonal
La	Orthorhombic	Tetragonal
Pr	Orthorhombic	Tetragonal
Nd	Orthorhombic	Orthorhombic
Y	Hexagonal	Orthorhombic
Gd	Hexagonal	Orthorhombic
Tb	Hexagonal	Orthorhombic
Dy	Hexagonal	Orthorhombic
Ho	Hexagonal	Orthorhombic
Er	Hexagonal	Hexagonal
Tm	Hexagonal	Hexagonal

followed by annealing at $450 \rightarrow 600^{\circ}$ C for approximately 24 hours. The structure of their samples was determined by X-ray diffraction and then re-examined using the same technique after the samples had undergone a further heat treatment at 1600°C.

More recently there has been a significant amount of experimental evidence to show that rare-earth disilicides are not crystallographically stable and that defect structures, often with an ordering of silicon vacancies, are preferred, e.g. Auffret *et al.* (1990), Madar *et al.* (1990), Schobinger-Papamantellos *et al.* (1990) and Iandelli *et al.* (1979). For the heavy rare-earths 'disilicides' the largest silicon content is $\approx RESi_{1.85}$ (Auffret *et al.*, 1991). For Nd and Gd the phases in equilibrium with silicon are orthorhombic and exist in the composition range $RESi_{1.75}$ to $RESi_{1.9}$ (Houssay *et al.*, 1989). For Pr the instability of the disilicide has been proven (Dijkman (1982), Lambert-Andron *et al.*, (1991)) and the evidence for the crystallographic instability of CeSi₂ will be discussed in more detail in § 4.1. At the present time there is no evidence to suggest that LaSi₂ is crystallographically unstable other than the dimorphism as a



Figure 1.4: Ionic radii of the rare-earth elements (Lide, 1991). Y^{3+} and U^{4+} have been superimposed for comparison.

function of temperature. However there still remains some inconsistency in the nature of this dimorphism since Satoh & Asada (1970) report a tetragonal \rightarrow orthorhombic transition following high temperature annealing of their LaSi₂ sample, contrary to Table 1.1. The same authors report a ThSi₂-type \rightarrow GdSi₂-type structure change for LaSi_x with increasing silicon deficiency.

Similar crystal instabilities are also observed for YSi₂ (Button *et al.*, 1990) and USi₂ (Sasa & Uda, 1976) whose ionic radii are of a similar size to that of the lanthanides, illustrated in Fig. 1.4. A more detailed discussion of the factors influencing the crystallographic instability of CeSi₂ and the other rare-earth silicides will be presented in § 6.1. For the moment it is evident that the size of the rare-earth ion is of great importance in determining the stable crystallographic structure of rare-earth 'disilicides'. As the ionic radius of the rare-earth ion decreases the silicide $RESi_x$ with the largest x is successively tetragonal, orthorhombic and then hexagonal.

1.2 Physical properties of rare-earth alloys

A thorough introduction to the general properties of rare-earth metals and alloys may be found in the reviews of Coqblin (1977), Buschow (1979) and Pierre (1982). Some of the important properties that are relevant to the following chapters are summarized briefly below.

Magnetism of rare-earth metals

The normal electronic configuration of the rare-earth elements is $[Xe]4f^n5d^16s^2$ where *n* is an integer (n = 1, 2, ..., 14). In the metallic state the 5*d* and 6*s* energy levels are mixed to give the conduction band whereas the inner 4*f* orbitals are more localized (Freeman, 1972). The magnetic moment of rare-earth ions originates from the presence of unpaired electrons in the 4*f* electronic orbital and due to the localization of this orbital, in the solid state the magnetism of the rare-earths is closest to that of an assembly of free ions. To a good approximation the high temperature magnetic susceptibilities of the rare-earth metals follows the Curie-Weiss law and the coupling of the spin *S* and orbital *L* angular momentum of the 4*f* electrons to give a total angular momentum *J*, is generally well predicted using Hund's rules. The magnetic moment of the ion is given by

$$\mu = \mu_B g_J \sqrt{J(J+1)} \tag{1.1}$$

where μ_B is the Bohr magneton and g_J is the Landé splitting factor, defined by

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$
(1.2)

Important magnetic interactions

In a solid the 4f electrons on a rare-earth ion are subject to a variety of interactions with the neighbouring ions that may be broadly classified into two categories (Jensen & Mackintosh, 1991). Two-ion interactions that couple directly the 4f electrons on neighbouring ions, and single-ion interactions that act independently at each ionic site such that the state of the 4f electrons at a particular site is unaffected by the magnetic state of its neighbours. The two-ion interactions in rare-earth metals are the classical *Coulomb interaction* and the quantum-mechanical *exchange interaction*. As a result of the negligible direct overlap of neighbouring 4f orbitals, the dominant exchange interaction between the 4f electrons on neighbouring rare-earth ions is an indirect exchange interaction via a polarization of the conduction electrons. This is known as the *RKKY interaction* and is described in more detail in § 2.3.

The important single-ion interaction in rare-earth metals is the electrostatic interaction between the ions. Normally the electrostatic potential due to the neighbouring ions is summed up to form an effective electric field that acts on the particular ion, known as the *crystalline electric-field*. This single-ion effect can not give rise to cooperative phenomena between the spins on the different ions but does reflect the crystal symmetry of the ions. In rare-earth metals and alloys it is the RKKY interaction that determines the type of ordering of the magnetic moments in the crystal, whereas it is the crystalline electric-field that influences the alignment of the ordered moments along a particular crystal axis direction.

Specific-heat capacity and Intermediate Valency

The specific-heat capacity (c_v) is an important physical property of any system since its measurement yields information on the existence of phase transitions and the electronic band-structure of a solid. The former may easily be understood from the definition of c_v as the energy required to raise a body through unit temperature, i.e.

$$c_{v} = \left(\frac{\partial U}{\partial T}\right)_{v} \tag{1.3}$$

U is the internal energy of the system and from the differential form of the First law of thermodynamics,

$$dU = TdS - PdV \tag{1.4}$$

where S is the entropy, P the pressure and V the volume of a system, then for a system at constant volume

$$c_{v} = T \left(\frac{\partial S}{\partial T}\right)_{v} \tag{1.5}$$

Consequently changes in the entropy of a system as a result of an ordering/disordering process at a phase transition will be reflected in the specific-heat capacity of the solid.

Such discontinuities in c_v can be used to indicate the onset of magnetic order in CeSi_x samples.

For rare-earth metals and the situation where there are no magnetic phase transitions, the specific-heat capacity at low temperatures may be analyzed (Coqblin, 1977) by

$$c_{\upsilon} = \gamma T + \beta T^3 + \delta(T) \tag{1.6}$$

The first term in (1.6) is the electronic specific-heat, the second term is the phonon contribution and $\delta(T)$ represents the contribution from spin-fluctuations and correlation phenomena. The latter is only significant at very low temperatures and may be assumed to be negligible here since the magnetic moment of the cerium ions is small. The coefficient γ is related to the density of electronic states at the Fermi level via

$$\gamma = \frac{2\pi^2}{3} k_B^2 Ng\left(\varepsilon_F\right) \tag{1.7}$$

where $g(\varepsilon_F)$ is the density of states at the Fermi level for one spin direction and N the number of conduction electrons per mole. It is common to use the magnitude of the coefficient γ to classify materials as *intermediate valence* ($\gamma = 100 \rightarrow 400$ mJ mol⁻¹ K²) or *heavy-fermion* ($\gamma > 400$ mJ mol⁻¹ K²) compounds (Stewart, 1984). The enhancement of γ is taken as an indication of a large density of states at the Fermi level due to the proximity of the narrow 4*f*-band. In such cases the possibility of mixing of the 4*f* and conduction electrons leads to a non-integral occupation of the 4*f*-band, commonly referred to as 'intermediate valency' (Buschow, 1979).

Electrical resistivity of rare-earth alloys

The electrical resistivity is another physical property that yields valuable information concerning the state and surroundings of the 4f electrons in a rare-earth alloy. It is a very sensitive probe to changes within the crystal lattice and in the correlations between the spins of the 4f electrons, and thus may be used to indicate the occurrence of phase transitions within a system, both crystallographic and magnetic. Matthiesen's rule states that the total resistivity (ρ) of a solid may be subdivided into three main contributions,

$$\rho = \rho_{res} + \rho_{ph} + \rho_m \tag{1.8}$$



Figure 1.5: Schematic curve of $\rho(T)$ for a typical magnetic rare-earth metal such as Gadolinium, courtesy of Coqblin (1977).

The resistance arises from the scattering of conduction electrons by impurities (ρ_{res}), phonons (ρ_{ph}) and the disordered component of the 4f electron magnetic moment (ρ_m).

Fig. 1.5 illustrates a schematic curve of the electrical resistivity as a function of temperature for a typical rare-earth metal (Coqblin, 1977). In the non-magnetic rareearth metals, Lanthanum, Ytterbium and Lutetium, the resistivity would have the finite value ρ_{res} at 0K and increase continuously with increasing temperature without peaks or other anomalies. However, for the magnetic rare-earths the thermal variation of ρ may be divided into two well-separated regions. At low temperatures ρ generally increases rapidly, often with some discontinuities (e.g. position A in Fig. 1.5), due to the thermal destruction of magnetic order within the solid. At higher temperatures there is normally a change in the gradient of $\rho(T)$, sometimes accompanied by a peak in ρ (e.g. position B), after which $\rho(T)$ is governed by the phonon contribution. For temperatures higher than the Debye temperature it remains approximately linear with temperature and this region, within which the magnetic resistivity ρ_m remains constant and equal to ρ_m^0 , is referred to as the paramagnetic region. ρ_m^0 may be determined by extrapolation of the high temperature linear resistivity to 0K.

The temperature dependence and anomalies in the electrical resistivity of CeSi_x will be presented and discussed in more detail in § 4.5.

Chapter 2

Theory

The technique of neutron scattering is an invaluable tool for probing the microscopic behaviour of condensed matter systems, most significantly the magnetic properties of such systems. The neutron is an appropriate probe due to its intrinsic properties:-

- The mass of the neutron results in the de Broglie wavelength of thermal neutrons being of the order 1 → 3Å. This is of the same order of magnitude as the interatomic distances in solids and the interference effects that consequently occur yield information on both the nuclear and magnetic structure of the scattering system.
- The neutron is a neutral particle and thus can penetrate deeply into the target and close to the nuclei without having to overcome a Coulomb barrier due to electrostatic forces.
- The neutron has an intrinsic magnetic moment which interacts with the unpaired electrons in magnetic atoms.
- The energy of thermal neutrons is of the same order as that of many excitations in condensed matter. Thus the analysis of the energy of the inelastically scattered neutrons gives information on the dynamical processes occurring in solids due to the coherent motion of the nuclei (phonons) or that of the magnetic moments (magnons).

The following short review of the theory of neutron scattering is divided into two parts. The aim of the first section is to provide a background to the formulae used in the description of the neutron-target interaction and the scattering cross sections. The second section illustrates how in spin polarized neutron scattering the scattering vector and neutron spin polarization dependences of the cross sections may be exploited by the technique of neutron x-y-z spin polarization analysis to unambiguously separate the paramagnetic scattering and antiferromagnetic scattering from all other scattering contributions, independently of any model assumptions. Reviews of the theory of neutron scattering may be found in numerous texts, e.g. Marshall & Lovesey (1971), and for a detailed description of spin polarized neutron scattering, Neumann (1990). A thorough description of the technique of x - y - z neutron spin polarization analysis is given by Schärpf & Capellmann (1993).

2.1 Scattering theory

In a neutron scattering experiment the physical quantity that is measured is the partial differential scattering cross section defined by

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{\begin{pmatrix} \text{number of neutrons scattered per second into the solid} \\ \text{angle } d\Omega \text{ in the direction } (\theta, \phi) \text{ with final energy} \\ \text{between } E_{\lambda_f} \text{ and } E_{\lambda_f} + dE \end{pmatrix}}{\Phi d\Omega dE}$$
(2.1)

where Φ is the flux of incident neutrons. For a spin polarized neutron scattering event whose geometry is shown in Fig. 2.1 and in which the incident neutron changes from the state $|k_i\nu_i\rangle$ to the state $|k_f\nu_f\rangle$ and the target changes from the state $|\lambda_i\rangle$ to $|\lambda_f\rangle$, the partial differential scattering cross section is given by

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{k_f}{k_i} \left(\frac{m_n}{2\pi\hbar^2}\right)^2 \sum_{\lambda_i \nu_i} p_{\lambda_i} p_{\nu_i} \sum_{\lambda_j \nu_j} |\langle k_f \nu_f \lambda_f | \hat{V} | k_i \nu_i \lambda_i \rangle|^2 \\ \times \delta \left(\hbar\omega + E_{\lambda_i} - E_{\lambda_j}\right)$$
(2.2)

where

$$\hbar\omega = \frac{\hbar^2}{2m_n} \left(k_i^2 - k_f^2\right) = E_{\lambda_i} - E_{\lambda_f}$$
(2.3)

and p_{λ_i} is the probability that the target is in an initial state λ_i , p_{ν_i} is the probability distribution of the polarization of the incident neutrons, V is the interaction potential



Figure 2.1: Geometry of the neutron scattering event, courtesy of Marshall & Lovesey (1971).

between the neutron and the target, and the transition probability is given by Fermi's Golden rule. The total interaction potential V is the sum of the nuclear (V_n) and magnetic (V_m) interaction potentials, the components of which are described briefly below.

The nuclear interaction potential V_n

It has been shown experimentally that the nucleon-nucleon interaction between the incident neutron and the target nuclei is very short range ($\approx 1.5 \times 10^{-15}$ m) and the nuclear radius is of the order of $\approx 10^{-14}$ m. Both are considerably smaller than the wavelength of thermal neutrons and consequently the neutron-nucleus scattering is isotropic and within the first Born approximation may be characterized by a single parameter *b* known as the *scattering length*. The nuclear interaction potential between a neutron at position *r* and a single nucleus at the position R_j is described by the

Fermi pseudo potential

$$V_n(\boldsymbol{r},\boldsymbol{R}_j) = \frac{2\pi\hbar^2}{m_n} b_j \delta\left(\boldsymbol{r}-\boldsymbol{R}_j\right)$$
(2.4)

where b_j is the scattering length of the nucleus at position R_j . The scattering length may be complex and the real part may be either positive or negative depending on the energy of the incident neutron and the particular nucleus involved in the scattering. b is different not only for each atom but also for each isotope and furthermore it depends on the relative coupling between the neutron spin $\nu = \frac{1}{2}\sigma_n$ and the nuclear spin ξ of the isotope.

To allow for the spin dependence of the neutron-nucleus interaction, the concept of a scattering length operator \hat{b} is used. For a single nucleus this would be defined by

$$\hat{b} = A + B\hat{\xi}.\hat{\sigma}_n \tag{2.5}$$

where the coefficients A and B are determined from the requirement that \tilde{b} should have eigenvalues $b_{+} = \xi + \frac{1}{2}$ and $b_{-} = \xi - \frac{1}{2}$ for the two possible states of the total spin. The variation of \hat{b} from one nucleus to another within the target as a result of the nuclear spin or the presence of isotopes or both, gives rise to two types of neutron scattering known as *coherent* and *diffuse* scattering. The coherent scattering arises from the mean scattering potential \bar{b} . In contrast the diffuse scattering is the result of the random distribution of the deviations of the scattering lengths from their mean value (*disorder* scattering) and the fluctuations of the nuclear spins (*incoherent* scattering), both of which within the field and temperature range of interest here cannot give rise to interference effects.

The magnetic interaction potential V_m

The magnetic interaction between the incident neutrons and the unpaired electrons in the target atoms is a consequence of the energy of the neutron magnetic moment μ_n in the magnetic field H arising from the unpaired electrons,

$$V_m = -\mu_n \cdot H \tag{2.6}$$

The magnetic field H has a contribution from the magnetic dipole (spin contribution) and the momentum of the electrons that gives rise to a current (orbital contribution).

The operator corresponding to the magnetic dipole moment of the neutron is denoted by

$$\hat{\boldsymbol{\mu}}_{\boldsymbol{n}} = -\gamma \boldsymbol{\mu}_{N} \hat{\boldsymbol{\sigma}}_{\boldsymbol{n}} \tag{2.7}$$

where the coefficient $\gamma = 1.9132$, μ_N is the nuclear magneton and $\hat{\sigma}_n$ is the Pauli spin operator for the neutron. Similarly the operator corresponding to the magnetic dipole moment of the electron is denoted by

$$\hat{\boldsymbol{\mu}}_{\boldsymbol{e}} = -2\mu_B \hat{\boldsymbol{s}}_{\boldsymbol{e}} \tag{2.8}$$

where μ_B is the Bohr magneton and \hat{s}_e is the spin angular momentum operator for the electron in units of \hbar . Denoting \hat{p}_e to be the momentum operator for the electron, it may be shown that if R is the distance from the electron to the point at which the field is measured, the magnetic interaction potential operator is given by

$$\hat{V}_{m} = -\gamma \mu_{N} \hat{\sigma}_{n} \hat{H} \\
= \frac{\mu_{0}}{4\pi} \gamma \mu_{N} \left\{ 2\mu_{B} \hat{\sigma}_{n} \text{.curl} \left(\frac{\hat{s}_{e} \times R}{|R|^{3}} \right) - \frac{2\mu_{B}}{\hbar} \left(\hat{p}_{e} \cdot \frac{\hat{\sigma}_{n} \times R}{|R|^{3}} + \frac{\hat{\sigma}_{n} \times R}{|R|^{3}} \cdot \hat{p}_{e} \right) \right\}$$
(2.9)

Nuclear scattering from crystals

For purely nuclear scattering the interaction potential between the neutrons and target is taken to be of the form

$$\hat{V}(r) = \hat{V}_n(r) = \sum_j \hat{V}_{nj}(r - R_j)$$
 (2.10)

where R_j is the position vector of the j^{th} scattering nucleus. For the scattering of unpolarized neutrons (2.2) may be shown to be

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{k_f}{k_i} \left(\frac{m_n}{2\pi\hbar^2}\right)^2 \sum_{\lambda_i \lambda_f} p_{\lambda_i} |\langle \lambda_f| \sum_j \hat{V}_n(\kappa) e^{i\kappa \cdot R_j} |\lambda_i\rangle|^2 \\ \times \delta \left(\hbar\omega + E_{\lambda_i} - E_{\lambda_f}\right)$$
(2.11)

where

$$\hat{V}_n(\kappa) = \int d\mathbf{r} e^{i\boldsymbol{\kappa}.\boldsymbol{r}} \hat{V}_{nj}(\boldsymbol{r})$$
(2.12)

By writing the δ -function in (2.11) within integral form, the sum over the final states λ_f may be performed by closure. The average over the initial states λ_i , with probability p_{λ_i} , involves an average firstly over the nuclear spin orientations and isotope

distributions and secondly an average over the initial states of the target whose distribution is given by a Boltzmann distribution. Denoting by angular brackets $\langle \ldots \rangle$ the thermal averaging, i.e.

$$\langle \ldots \rangle = \sum_{\lambda_i} \frac{e^{-\frac{B_{\lambda_i}}{k_B T}}}{\sum_{\lambda_i} e^{-\frac{B_{\lambda_i}}{k_B T}}} \langle \lambda_i | \ldots | \lambda_i \rangle$$
(2.13)

then within this notation the partial differential cross section may be written in general form as

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{k_f}{k_i} \left(\frac{m_n}{2\pi\hbar^2}\right)^2 \frac{1}{2\pi\hbar} \times \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{j,j'} \overline{\hat{V}_{n'}^{\dagger}(\kappa)} \hat{V}_{n}(\kappa) \langle e^{-i\kappa.\hat{R}_{j'}(0)} e^{i\kappa.\hat{R}_{j}(t)} \rangle \qquad (2.14)$$

Assuming that there is no correlation between the b values of different nuclei, i.e.

$$\overline{b_{j'}b_j} = |\overline{b}|^2 \qquad j' \neq j$$

$$\overline{b_{j'}b_j} = \overline{|b|^2} \qquad j' = j \qquad (2.15)$$

then from (2.4),

$$\overline{\hat{V}_{n'}^{\dagger}(\kappa)\hat{V}_{n}(\kappa)} = \left(\frac{2\pi\hbar^{2}}{m_{n}}\right)^{2} \left\{ |\bar{b}|^{2} + \delta_{j,j'} \left[|\bar{b}|^{2} - |\bar{b}|^{2} \right] \right\}$$
(2.16)

Introducing the coherent (σ_{coh}) and incoherent (σ_{inc}) nuclear scattering cross sections

$$\sigma_{coh} = 4\pi |\bar{b}|^2$$

$$\sigma_{inc} = 4\pi \left\{ \overline{|b|^2} - |\bar{b}|^2 \right\}$$
(2.17)

then the two contributions to the partial differential cross section (2.14) may be written as

$$\left(\frac{\partial^2 \sigma_{coh}}{\partial \Omega \partial E}\right) = N \frac{k_f}{k_i} \frac{\sigma_{coh}}{4\pi} S_{coh}(\kappa, \omega)$$
(2.18)

$$\left(\frac{\partial^2 \sigma_{inc}}{\partial \Omega \partial E}\right) = N \frac{k_f}{k_i} \frac{\sigma_{inc}}{4\pi} S_{inc}(\kappa, \omega)$$
(2.19)

where N is the total number of scattering nuclei,

$$S_{coh}(\kappa,\omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{j,j'} \langle e^{-i\kappa \cdot \hat{R}_{j'}(0)} e^{i\kappa \cdot \hat{R}_{j}(t)} \rangle$$
(2.20)

and

$$S_{inc}(\kappa,\omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{j} \langle e^{-i\kappa \cdot \hat{R}_{j}(0)} e^{i\kappa \cdot \hat{R}_{j}(t)} \rangle$$
(2.21)

 $S_{coh}(\kappa,\omega)$ is known as the scattering function of the system and $S_{inc}(\kappa,\omega)$ the incoherent scattering function.



Figure 2.2: Position of the j^{th} nucleus; • = equilibrium position, • = actual (instantaneous) position.

Coherent nuclear scattering from crystals

At any finite temperature the thermal motion of the j^{th} nucleus will cause it to be displaced from its equilibrium position j. Its instantaneous position will be defined by

$$\boldsymbol{R_j} = \boldsymbol{j} + \boldsymbol{u_j} \tag{2.22}$$

where j is a crystal lattice vector and u_j is the displacement of the nucleus from its equilibrium position, as shown in Fig. 2.2. For a Bravais crystal (i.e. one atom per unit cell) the correlation between the positions of the nuclei j and j' depends only on (j - j'). Setting j' = 0 and using $R_j(t) = j + u_j(t)$, it may be shown that

$$\sum_{j,j'} \langle e^{-i\kappa \cdot \hat{R}_{j'}(0)} e^{i\kappa \cdot \hat{R}_{j}(t)} \rangle = N \sum_{j} e^{i\kappa \cdot j} \langle e^{-i\kappa \cdot \hat{u}_0(0)} e^{i\kappa \cdot \hat{u}_j(t)} \rangle$$
(2.23)

and

$$\sum_{j} \langle e^{-i\kappa \cdot \hat{R}_{j}(0)} e^{i\kappa \cdot \hat{R}_{j}(t)} \rangle = N \langle e^{-i\kappa \cdot \hat{u}_{0}(0)} e^{i\kappa \cdot \hat{u}_{0}(t)} \rangle$$
(2.24)

where $\hat{u}_j(t)$ is the Heisenberg operator for u_j . Using the probability function for a harmonic oscillator, the thermal averages $\langle \ldots \rangle$ in (2.23) and (2.24) may be evaluated and it may be shown that the coherent elastic scattering from a Bravais crystal is given by

$$\left(\frac{d\sigma_{coh}}{d\Omega}\right)_{el} = \frac{\sigma_{coh}}{4\pi} N \frac{(2\pi)^3}{v_0} e^{-2W(\kappa)} \sum_{q} \delta(\kappa - q)$$
(2.25)

where q is a reciprocal lattice vector and

$$2W(\kappa) = \langle \{\kappa. u_0(0)\}^2 \rangle \tag{2.26}$$

The exponential term $2W(\kappa)$ is known as the *Debye-Waller factor* and it represents the mean square displacement of a nucleus multiplied by κ^2 .



Figure 2.3: Position vectors of the atom j, d in a non-Bravais crystal; • = equilibrium position, o = actual (instantaneous) position.

For the coherent nuclear elastic scattering from a non-Bravais crystal, the equilibrium position of the d^{th} atom in the unit cell is denoted by d. The position of the atom d in the crystal is

$$\boldsymbol{R}_{jd} = \boldsymbol{j} + \boldsymbol{d} + \boldsymbol{u} \begin{pmatrix} \boldsymbol{j} \\ \boldsymbol{d} \end{pmatrix}$$
(2.27)

where j + d is the equilibrium position of the atom and $u\binom{j}{d}$ is the displacement from equilibrium, as illustrated in Fig. 2.3. Generally there will be a different type of nucleus at each d position and the mean value of the scattering length (i.e. the average over isotopes and nuclear spin) is different for each d position and denoted \overline{b}_d . It may be shown that

$$\left(\frac{d\sigma_{coh}}{d\Omega}\right)_{el} = N \frac{(2\pi)^3}{v_0} \sum_{q} \delta(\kappa - q) |F_N(\kappa)|^2$$
(2.28)

where

$$F_N(\kappa) = \sum_d \bar{b}_d e^{i\kappa \cdot d} e^{-W_d(\kappa)}$$
(2.29)

and the Debye-Waller factor is given by

$$W_d(\kappa) = \frac{1}{2} \langle \{\kappa. u \begin{pmatrix} j \\ d \end{pmatrix} \}^2 \rangle$$
(2.30)

 $F_N(\kappa)$ is known as the nuclear unit cell structure factor.

Equations (2.25) and (2.28) illustrate that there is only a coherent nuclear scattering contribution when

$$\kappa = k_i - k_f = q \tag{2.31}$$

where q is a reciprocal lattice vector. This condition is equivalent to Bragg's law for X-ray scattering and the coherent nuclear scattering contribution is referred to as the nuclear Bragg scattering. For the diffraction profiles that will be presented in Chapter 3, above the magnetic ordering temperature it is the $\left(\frac{d\sigma_{coh}}{d\Omega}\right)_{el}$ contribution that determines the reflections observed in the diffraction profile.

Magnetic scattering from crystals

The contribution to the magnetic scattering of neutrons by a target is given by

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{k_f}{k_i} \left(\frac{m_n}{2\pi\hbar^2}\right)^2 \sum_{\lambda_i \nu_i} p_{\lambda_i} p_{\nu_i} \sum_{\lambda_f \nu_f} |\langle k_f \nu_f \lambda_f | \hat{V}_m | k_i \nu_i \lambda_i \rangle|^2 \times \delta \left(\hbar\omega + E_{\lambda_i} - E_{\lambda_f}\right)$$
(2.32)

with \hat{V}_m given by (2.9). The evaluation of $\langle k_f | \hat{V}_m | k_i \rangle$, i.e. integrating over the space coordinates of the neutron, may be shown to give

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = (\gamma r_0)^2 \frac{k_f}{k_i} \sum_{\lambda_i \nu_i} p_{\lambda_i} p_{\nu_i} \sum_{\lambda_f \nu_f} |\langle \nu_f \lambda_f | \hat{\sigma}_n . \hat{Q}_\perp | \nu_i \lambda_i \rangle|^2 \\ \times \delta \left(\hbar \omega + E_{\lambda_i} - E_{\lambda_f} \right)$$
(2.33)

where r_0 is the classical electron radius and

$$\hat{Q}_{\perp} = \sum_{j} e^{i\kappa \cdot r_{ej}} \left\{ \frac{\kappa}{\kappa} \times \left(\hat{s}_{ej} \times \frac{\kappa}{\kappa} \right) + \frac{i}{\hbar\kappa} \left(\hat{p}_{ej} \times \frac{\kappa}{\kappa} \right) \right\}$$
(2.34)

with r_{ej} the position vector of the j^{th} electron. The operator \hat{Q}_{\perp} is the component of \hat{Q} that is perpendicular to the scattering vector, i.e.

$$\hat{Q}_{\perp} = \hat{Q} - \left(\hat{Q}.\frac{\kappa}{\kappa}\right)\frac{\kappa}{\kappa}$$
(2.35)

and Q is the Fourier transform of M(r), the total magnetization of the unpaired electrons in the ion due to their spin and orbital motion. From (2.34) it is evident that only the components of the magnetic interaction potential that are perpendicular to the scattering vector give rise to magnetic neutron scattering.

It may be shown that for the scattering from a magnetic ion which possesses both spin and orbital angular momentum, if the mean radius of the wave function of the unpaired electrons is much less than $|\kappa|^{-1}$ (a condition generally well satisfied for the rare-earth ions) then within the *dipole approximation*, the operator \hat{Q} may be replaced by

$$\hat{Q} \approx \frac{1}{2} g_J f(\kappa) \sum_{j,d} e^{i\kappa \cdot R_{jd}} \hat{J}_{jd}$$
(2.36)

where $f(\kappa)$ is the magnetic form-factor of the ion and \hat{J}_{jd} is the total angular momentum operator of the ion j, d. Within the dipole approximation the magnetic form-factor is given by

$$f(\kappa) = \frac{g_S}{g_J} \zeta_0 + \frac{g_L}{g_J} \left(\zeta_0 + \zeta_2 \right) \tag{2.37}$$

where $g_J = g_S + g_L$,

$$g_{S} = 1 + \frac{S(S+1) - L(L+1)}{J(J+1)}$$
$$g_{L} = \frac{1}{2} + \frac{L(L+1) - S(S+1)}{2J(J+1)}$$
(2.38)

and

$$\zeta_n = 4\pi \int_0^\infty j_n(\kappa r) \rho_e(r) r^2 dr \qquad (2.39)$$

 g_J is the Landé splitting factor, $j_n(\kappa r)$ is a spherical Bessel function of order n and $\rho_e(r)$ is the normalized density of the unpaired electrons averaged over all directions in space. Within the dipole approximation it may be shown that for the scattering of unpolarized neutrons from a Bravais crystal with identical magnetic ions,

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = (\gamma r_0)^2 N \frac{k_f}{k_i} \left\{ \frac{1}{2} g_J f(\kappa) \right\}^2 e^{-2W(\kappa)} \times \sum_{\alpha\beta} \left(\delta_{\alpha\beta} - \frac{\kappa_\alpha}{\kappa_\alpha} \frac{\kappa_\beta}{\kappa_\beta} \right) S^{\alpha\beta}(\kappa, \omega)$$
(2.40)

with

$$S^{\alpha\beta}(\kappa,\omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{j,j'} e^{i\kappa \cdot (R_j - R_{j'})} \langle \hat{J}_{j'}^{\alpha}(0) \hat{J}_{j}^{\beta}(t) \rangle$$
(2.41)

and for which $e^{-2W(\kappa)}$ is the Debye-Waller factor and \hat{J}_j^{β} is the operator corresponding to the β component of the total spin of the ion j. $S^{\alpha\beta}(\kappa,\omega)$ is the Fourier transform in space and time of the spin-spin correlation function $\langle \hat{J}_{j'}^{\alpha}(0)\hat{J}_{j}^{\beta}(t)\rangle$ and in physical terms, it represents the probability that, if one moment at the site j' has some specified vector value at time zero then the moment at site j has some other specified value at time t. By the use of the fluctuation-dissipation theorem the correlation function can be related to the imaginary part of the magnetic susceptibility according to

$$S^{\alpha\beta}(\kappa,\omega) = \frac{1}{\pi} \frac{1}{1 - e^{\frac{-\hbar\omega}{k_B T}}} \operatorname{Im}\left(\chi^{\alpha\beta}(\kappa,\omega,T)\right)$$
(2.42)

Then by the use of the Kramers-Kronig relation the imaginary part of the susceptibility can be expressed as a function of the real part by

$$\operatorname{Re}\left(\chi^{\alpha\beta}(\kappa,T)\right) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\operatorname{Im}\left(\chi^{\alpha\beta}(\kappa,\omega,T)\right)}{\hbar\omega} d\omega \qquad (2.43)$$

In the limit of zero scattering vector the real part of the susceptibility approaches the value of the bulk susceptibility χ_{bulk}

$$\sum_{\alpha,\beta} \operatorname{Re}\left(\chi^{\alpha\beta}\left(\kappa=0,T\right)\right) = \chi_{\text{bulk}}$$
(2.44)

Hence the relations (2.42) and (2.43) are of importance since they enable the neutron scattering measurements to be related to the physical measurement of the sample magnetization, thus providing a useful check of the consistency of the experimental neutron scattering data.

For work described in the following chapters, it is of use to define a magnetic propagation vector (q_m) that characterizes a long range magnetically ordered structure. q_m allows a magnetic moment M_n at the lattice site n and with position vector R_n to be expressed in terms of another moment M_0 at the position R_0 that is taken as a reference and used to define a unique direction. It is defined by

$$M_n = M_0 e^{iq_m \cdot (R_n - R_0)} \tag{2.45}$$

2.2 Theory of x - y - z spin polarization analysis

The technique of using spin polarized neutron scattering and spin polarization analysis to separate the paramagnetic and antiferromagnetic scattering from all other scattering contributions has been described by Moon *et al.* (1969), Schärpf (1985) and Schärpf & Capellmann (1993) for the specific exploitation of neutron spin polarization analysis on a multidetector instrument such as the spectrometer D7. This technique exploits the dependence of the scattering cross sections on the scattering vector κ and the axis of quantization *e*. The latter is determined by the direction of the magnetic guide field at the sample and defines the spin polarization of the incident neutrons, *P*. As discussed in detail by Neumann (1990), such dependences may be summarized by three rules:-

- Only those parts of the vector component of the nuclear interaction potential that are perpendicular to e give rise to nuclear scattering with a flip of the neutron spin in the scattering process.
- Only the component of the magnetic interaction potential that is perpendicular to κ can give rise to magnetic scattering.
- The component of the magnetic interaction potential parallel to e gives rise to non-spin flip magnetic scattering whereas the component perpendicular to e
results in neutron spin flip scattering.

As such, both the coherent scattering and isotopic incoherent scattering contributions are entirely non-spin flip scattering contributions. The nuclear spin incoherent scattering gives contributions to both the spin flip and non-spin flip measured cross sections, as described below.

Schärpf & Capellmann (1993) have given a complete description of the x - y - zdifference method with polarized neutrons and how this may be used to separate the coherent, spin incoherent and magnetic scattering cross sections in a multidetector instrument, such as D7 at the ILL. Here, the main results of their paper will be described and related to the measurements that will be presented in Chapter 3. Firstly the neutron energy transfer during the scattering process is redefined such that (2.3) becomes

$$\omega = \frac{\hbar^2}{2m_n} \left(k_i^2 - k_f^2 \right) = E_{\lambda_i} - E_{\lambda_f}$$
(2.46)

The different types of scattering cross section that contribute to the total observed cross section are defined by

$$\frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega} = \frac{k_f}{k_i} \frac{2}{3} \left(\frac{\gamma r_0}{2}\right)^2 f^2(\kappa) M(\kappa, \omega)$$
(2.47)

$$\frac{\partial^2 \sigma_{inc}^{spin}}{\partial \Omega \partial \omega} = \frac{k_f}{k_i} B^2 S_{inc}(\kappa, \omega)$$
(2.48)

$$\frac{\partial^2 \sigma_{inc}^{isotop}}{\partial \Omega \partial \omega} = \frac{k_f}{k_i} \left(\overline{A^2} - \overline{A}^2 \right) S_{inc}(\kappa, \omega)$$
(2.49)

$$\frac{\partial^2 \sigma_{coh}}{\partial \Omega \partial \omega} = \frac{k_f}{k_i} |\bar{b}|^2 S_{coh}(\kappa, \omega)$$
(2.50)

The term $M(\kappa, \omega)$ in (2.47) is the magnetic part of the dynamical scattering function and is equivalent to $S^{\alpha\beta}(\kappa, \omega)$ in (2.40). The remaining terms in these equations have been described previously in (2.5). Equations (2.47) \rightarrow (2.50) represent the magnetic scattering, the nuclear spin incoherent scattering, the isotope incoherent scattering and the coherent scattering respectively. Implicit in the derivation of these results is that there are no correlations between the nuclear spins and the electron magnetic moments, there is no nuclear polarization, no nuclear magnetic interference term and only on site correlation between the nuclear spins (Schärpf & Capellmann, 1993). These assumptions are valid at the temperatures and fields of interest here.



Figure 2.4: Scattering geometry for D7.

For a spectrometer such as D7 for which the scattering vector is defined to lie in the x - y plane, Schärpf & Capellmann show that for a powder sample, measurement of the spin flip (sf) and non-spin flip (nsf) scattering with the incident neutron spin polarization alternatively in the x, y and z directions yields the following experimental cross sections:-

$$\begin{pmatrix} \frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \end{pmatrix}_x^{sf} = \frac{1}{2} \frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega} \left(1 + \cos^2 \alpha \right) + \frac{2}{3} \frac{\partial^2 \sigma_{inc}^{spin}}{\partial \Omega \partial \omega} \\ \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_y^{sf} = \frac{1}{2} \frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega} \left(1 + \sin^2 \alpha \right) + \frac{2}{3} \frac{\partial^2 \sigma_{inc}^{spin}}{\partial \Omega \partial \omega} \\ \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_x^{sf} = \frac{1}{2} \frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega} + \frac{2}{3} \frac{\partial^2 \sigma_{inc}^{spin}}{\partial \Omega \partial \omega} \\ \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_x^{nsf} = \frac{1}{2} \frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega} \sin^2 \alpha + \frac{1}{3} \frac{\partial^2 \sigma_{inc}^{spin}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{inc}}{\partial \Omega \partial \omega} \\ \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_y^{nsf} = \frac{1}{2} \frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega} \cos^2 \alpha + \frac{1}{3} \frac{\partial^2 \sigma_{inc}^{spin}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{inc}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{inc}^{isotop}}{\partial \Omega \partial \omega} \\ \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_x^{nsf} = \frac{1}{2} \frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega} + \frac{1}{3} \frac{\partial^2 \sigma_{inc}^{spin}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{inc}^{isotop}}{\partial \Omega \partial \omega} \\ \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_x^{nsf} = \frac{1}{2} \frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega} + \frac{1}{3} \frac{\partial^2 \sigma_{inc}^{spin}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{inc}^{isotop}}{\partial \Omega \partial \omega} \\ \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_x^{nsf} = \frac{1}{2} \frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega} + \frac{1}{3} \frac{\partial^2 \sigma_{inc}^{spin}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{inc}^{isotop}}{\partial \Omega \partial \omega} \\ \end{array}$$
(2.51)

where α represents the angle between the scattering vector $\hat{\kappa}$ and the x direction, as shown in Fig. 2.4. By combining these measured cross sections it is possible to separate the different scattering contributions from one another. It may be easily verified from (2.51) that the following combination of measured cross sections gives directly the paramagnetic or antiferromagnetic scattering cross section,

$$\left(\frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega}\right)^{sf} = 2 \left[\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_x^{sf} + \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_y^{sf} - 2 \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_z^{sf} \right]$$
(2.52)

and similarly

$$\left(\frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega}\right)^{nsf} = 2 \left[2 \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_x^{nsf} - \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_x^{nsf} - \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_y^{nsf} \right]$$
(2.53)

Furthermore, one can obtain the spin incoherent scattering cross section by

$$\frac{\partial^2 \sigma_{inc}^{spin}}{\partial \Omega \partial \omega} = \frac{3}{2} \left[3 \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_{z}^{sf} - \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_{x}^{sf} - \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_{y}^{sf} \right]$$
(2.54)

and subtracting the cross sections obtained in this way in (2.52) (or equation (2.53)) and (2.54) from the measured cross section $\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_{z}^{nsf}$ gives

$$\frac{\partial^2 \sigma_{coh}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{inc}^{isotop}}{\partial \Omega \partial \omega} = \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_z^{nsf} - \frac{1}{2} \frac{\partial^2 \sigma_{para}}{\partial \Omega \partial \omega} - \frac{1}{3} \frac{\partial^2 \sigma_{inc}^{spin}}{\partial \Omega \partial \omega}$$
(2.55)

It is not possible to distinguish the coherent scattering from the isotope incoherent scattering. It is stressed that the x-y-z difference technique allows the unambiguous separation of the individual contributions to the total scattering. σ_{para} , σ_{inc}^{spin} and σ_{coh} are obtainable solely by combination of the observed scattering cross sections as shown in equations (2.52) \rightarrow (2.55). This technique involves no model assumptions whatsoever.

In the experiments that will be described in § 3.6, the spectrometer D7 has been operated in 'integral' mode whereby the observed spin flip and non-spin flip scattering intensities consist of the sum over all scattering events, both elastic and inelastic. Mathematically, the differential scattering cross section is obtained from the partial differential scattering cross section by the integral over all neutron energy transfers ω , as defined by

$$\frac{d\sigma}{d\Omega} = \int_{-\infty}^{+\infty} \frac{\partial^2 \sigma}{\partial \Omega \partial \omega} d\omega$$
(2.56)

Taking the magnetic scattering as an example, then from (2.47)

$$\frac{d\sigma}{d\Omega} \propto \int_{-\infty}^{+\infty} \frac{k_f(\omega)}{k_i} f^2(\kappa) M(\kappa, \omega) d\omega \qquad (2.57)$$

In performing the integral over all ω , the *principle of detailed balance* must be taken into consideration, i.e.

$$M(-\kappa, -\omega) = e^{-\frac{\omega}{\kappa_B T}} M(\kappa, \omega)$$
(2.58)

The transitions that contribute to $M(\kappa, \omega)$ are those in which the initial target state λ_i has energy ω less than the final energy state λ_f and thus the neutron loses energy in the scattering process. Conversely, the transitions that contribute to $M(-\kappa, -\omega)$ are those in which the neutron gains energy and the scattering system loses energy ω . The principle of detailed balance reflects that the probability of the system being initially

in the higher energy state is lower by the factor $\exp\left(-\frac{\omega}{k_BT}\right)$ than its probability of being in the lower energy state. From (2.57) and (2.58) it may clearly be seen that the differential scattering cross section is dependent on the energy of the incident neutrons and the temperature of the target. With these factors taken into consideration, the paramagnetic differential scattering cross sections corresponding to (2.52) and (2.53) but for which the integral over all neutron energy transfers has been performed, may be expressed by

$$\left(\frac{d\sigma_{para}}{d\Omega}\right)^{sf} = 2\left[\left(\frac{d\sigma}{d\Omega}\right)_{x}^{sf} + \left(\frac{d\sigma}{d\Omega}\right)_{y}^{sf} - 2\left(\frac{d\sigma}{d\Omega}\right)_{z}^{sf}\right]$$
(2.59)

and

$$\left(\frac{d\sigma_{para}}{d\Omega}\right)^{nsf} = 2\left[2\left(\frac{d\sigma}{d\Omega}\right)_{z}^{nsf} - \left(\frac{d\sigma}{d\Omega}\right)_{x}^{nsf} - \left(\frac{d\sigma}{d\Omega}\right)_{y}^{nsf}\right]$$
(2.60)

2.3 Indirect s - f exchange interaction

In rare-earth metals and alloys the 4f electrons remain well localized around the rareearth ion and there is negligible direct overlap of the 4f wavefunctions of neighbouring ions. Consequently the direct exchange interaction between 4f electrons on neighbouring lattice sites is insignificant. The mechanism generally considered responsible for magnetic ordering in the rare-earths is indirect exchange between the rare-earth ions via a polarization of the conduction electrons. The interaction is referred to as the *RKKY interaction* in recognition of Ruderman & Kittel (1954), Kasuya (1956) and Yosida (1957) who developed its mathematical description. An overview of the essential features and mathematics of the RKKY interaction is given below. The formulae presented will be used in § 6.3 to estimate the variation of the nearest and next-nearest neighbour exchange interaction coefficients of CeSi_x as a function of x. The interaction is described in a more rigorous manner in the original references and numerous texts, e.g. Kittel (1963), Coqblin (1977).

Physically the RKKY interaction may be understood in terms of a spin S_n , localized on the atom n, interacting with the conduction electrons and creating a spin polarization of the conduction electron density due to the different response of the conduction electrons to the spin 'up' ($|\uparrow\rangle$) or spin 'down' ($|\downarrow\rangle$) state of S_n . The conduction electron spin polarization subsequently interacts with a second spin S_m , localized on the atom m, thus producing an indirect exchange interaction between the spins S_n and S_m .

Hamiltonian for the s - f interaction

The interaction Hamiltonian for the exchange between the spin s of a conduction electron and the spin S of a localized f electron is taken to be of the form

$$\mathcal{H} = -\Gamma s.S \tag{2.61}$$

where Γ is an interaction constant that depends on the degree of overlap of the wavefunctions of the *s* and *f* electrons. For rare-earth metals where the spin-orbit coupling energy is much larger than k_BT and the energy of the crystalline-electric field splitting, the intrinsic spin *S* may be replaced by the projection $(g_J - 1)J$ of the spin on *J* inside the ground state. As first proposed by de Gennes (1962) the s - fexchange interaction Hamiltonian (2.61) may thus be written as

$$\mathcal{H} = -\Gamma \left(g_J - 1 \right) s. J \tag{2.62}$$

The justification for the form of (2.62) is the large amount of experimental data on rare-earth compounds that is well explained by such an interaction (Coqblin, 1977).

Denoting the total spin of the rare-earth ion at the position R_n in the metal J_n , the interaction between the localized electron on ion n and a conduction electron of spin s(r) is given by

$$\mathcal{H} = -(g_J - 1) \sum_n \Gamma(r - R_n) s(r) J_n \qquad (2.63)$$

where $\Gamma(r - R_n)$ is the interaction function. The conduction electrons in the metal are described by Bloch functions

$$|k\nu\rangle = \psi_{k\nu}(r) = e^{ik.r} u_k(r) |\nu\rangle = \psi_k(r) |\nu\rangle \qquad (2.64)$$

that are normalized per unit volume and for which $\psi_k(r)$ represents the spatial part of the wavefunction and $|\nu\rangle$ the spin part. In order to use second quantization representation we define the operators $\hat{c}^+_{k\nu}$ and $\hat{c}_{k\nu}$ that respectively create and annihilate a conduction electron of wavevector k and spin ν , thus

$$|k
u
angle=\hat{c}^+_{k
u}|0
angle$$

and

$$\hat{c}_{k\nu}|k\nu\rangle = |0\rangle \tag{2.65}$$

where $|0\rangle$ is the vacuum state (i.e. no electrons). To write the Hamiltonian (2.63) in second quantization form an expansion is performed within the complete basis of orthonormalized wavefunctions $|k\nu\rangle$. Using the completeness relation

$$\sum_{k,\nu} |k\nu\rangle\langle k\nu| = 1$$
(2.66)

we obtain

$$\mathcal{H} = \sum_{kk'\nu\nu'} |k'\nu'\rangle \langle k'\nu'|\mathcal{H}|k\nu\rangle \langle k\nu|$$
(2.67)

and substituting from (2.65),

$$\mathcal{H} = \sum_{kk'\nu\nu'} \hat{c}^{\dagger}_{k'\nu'} \hat{c}_{k\nu} \langle k'\nu' | \mathcal{H} | k\nu \rangle$$
(2.68)

Using (2.63) the average of \mathcal{H} over the Bloch functions defined by (2.64) is

$$\langle k'\nu'|\mathcal{H}|k\nu\rangle = -(g_J - 1)\sum_n \int d^3r \psi_{k'}^*(r)\Gamma(r - R_n)\psi_k(r)\langle \nu'|s(r).J_n|\nu\rangle \qquad (2.69)$$

Using the fact that $\psi_k(r)$ is a Bloch function

$$\psi_k(r) = e^{ik \cdot R_n} \psi_k(r - R_n) \tag{2.70}$$

and utilizing the ladder operators $\hat{s}^+(r)$, $\hat{s}^-(r)$, \hat{J}^+_n and \hat{J}^-_n such that

$$\hat{s}(r).\hat{J}_{n} = \hat{s}_{z}(r)\hat{J}_{z_{n}} + \frac{1}{2}\left[\hat{s}^{+}(r)\hat{J}_{n}^{-} + \hat{s}^{-}(r)\hat{J}_{n}^{+}\right]$$
(2.71)

then the Hamiltonian (2.68) may be written

$$\mathcal{H} = -(g_J - 1) \sum_{k,k',n} \Gamma(k',k) e^{i(k-k')R_n} \hat{J}_{n} \hat{s}_{k'k}$$
(2.72)

where

$$\Gamma(k',k) = \int d^3 r \psi_{k'}^*(r) \Gamma(r) \psi_k(r) \qquad (2.73)$$

and

$$\hat{s}_{\boldsymbol{z_{k'k}}} = \frac{1}{2} \left(\hat{c}_{k'\uparrow}^{+} \hat{c}_{k\uparrow} - \hat{c}_{k'\downarrow}^{+} \hat{c}_{k\downarrow} \right)$$

$$\hat{s}_{k'k}^{+} = \hat{c}_{k'\uparrow}^{+} \hat{c}_{k\downarrow}$$

$$\hat{s}_{k'k}^{-} = \hat{c}_{k'\downarrow}^{+} \hat{c}_{k\uparrow}$$
(2.74)

In practice the value of $\Gamma(k', k)$ and its dependence on k' and k is not well known. The RKKY theory makes the approximation that the conduction electrons may be considered to be free electrons (thus the Fermi surface of the metal is approximated by a sphere) and it considers a point interaction for $\Gamma(r)$, i.e.

$$\Gamma(\mathbf{r}) = \Gamma \delta(\mathbf{r}) \tag{2.75}$$

Thus $\Gamma(k',k) = \Gamma$. The constant Γ has the dimension [energy×volume].

Spin polarization of the conduction electron density

Within the free electron approximation the wavefunctions for the conduction electrons may be written as

$$|k^{0}\nu\rangle = \phi^{0}_{k\nu} = e^{ik.r}|\nu\rangle \tag{2.76}$$

The perturbed wavefunctions of the conduction electrons as a result of the s - finteraction may be calculated within second order perturbation theory via

$$\phi_{k\nu} = \phi_{k\nu}^{0} + \sum_{k',\nu'}^{\prime} \frac{\langle k^{0}\nu | \mathcal{H} | k'^{0}\nu' \rangle}{E_{k} - E_{k'}} \phi_{k'\nu'}^{0}$$
(2.77)

where the sum is over all the states $|k'^0\nu'\rangle$ except those for which $E_k = E_{k'}$. Defining the conduction electron spin density for the spin state ν by

$$\rho_{\nu}(r) = \sum_{k=0}^{k_{F}} \langle \nu || \phi_{k\nu}(r)|^{2} |\nu \rangle$$
(2.78)

with k_F^{ν} the Fermi wavevector for the conduction band for the spin state ν , then from (2.72) and (2.77) the polarization of the conduction electron spin density due to the s - f interaction may be shown (Coqblin, 1977) to be

$$\rho_{\pm}(\mathbf{r}) = N \mp \frac{(3N)^2}{E_F} \pi (g_J - 1) \Gamma \sum_{\mathbf{n}} F(2k_F |\mathbf{r} - \mathbf{R}_n|) J_{z_n}$$
(2.79)

with

$$F(x) = \frac{x\cos x - \sin x}{x^4} \tag{2.80}$$

and N the number of conduction electrons of one spin state per unit volume.

Resultant indirect exchange interaction

The spin polarization (2.79) produced by the spin S_n located on the ion n subsequently interacts with the spin S_m located on the ion m. Within second-order perturbation theory the interaction energy between the two spins S_n and S_m is given by

$$E = \sum_{k,k',\nu,\nu'} \frac{\langle k^{\circ}\nu | \mathcal{H} | k'^{\circ}\nu' \rangle \langle k'^{\circ}\nu' | \mathcal{H} | k^{\circ}\nu \rangle f_k(1 - f_{k'})}{E_k - E_{k'}}$$
(2.81)

where f_k is the Fermi-Dirac function,

$$f_{k} = \frac{1}{e^{(E_{k} - E_{F})/k_{B}T} + 1}$$
(2.82)

and the sum is made up of the occupied k states and the empty k' states. The result of such a calculation may be shown (Coqblin, 1977) to give

$$E = \frac{(3N)^2}{2E_F} \pi \Gamma^2 (g_J - 1)^2 \sum_{n,m(n \neq m)} J_n J_m F \left(2k_F |R_n - R_m| \right)$$
(2.83)

Recalling that for free electrons

$$E_F = \frac{\hbar^2 k_F^2}{2m_e}$$
(2.84)

and

$$N = \frac{k_F^3}{6\pi^2}$$
 (2.85)

then taking the spin degeneracy of each k state into consideration by defining Z = 2Nto be the total number of conduction electrons per unit volume, the expression for the interaction energy may be rewritten

$$E = \frac{m_e (3Z)^{\frac{4}{3}}}{4\hbar^2 \pi^{\frac{1}{3}}} \Gamma^2 (g_J - 1)^2 \sum_{n,m(n\neq m)} J_n J_m F\left(2\left(3\pi^2 Z\right)^{\frac{1}{3}} |R_n - R_m|\right)$$
(2.86)

Expressing the exchange interaction Hamiltonian by

$$\mathcal{H} = -\sum_{n,m} \mathcal{J}_{nm}^{RKKY} \boldsymbol{J}_n. \boldsymbol{J}_m$$
(2.87)

thus within the RKKY theory the indirect exchange parameter \mathcal{J}^{RKKY} for the interaction between the two spins J_n and J_m is given by

$$\mathcal{J}_{nm}^{RKKY} = -\frac{m_e(3Z)^{\frac{5}{3}}}{4\hbar^2 \pi^{\frac{1}{3}}} \Gamma^2 (g_J - 1)^2 F\left(2\left(3\pi^2 Z\right)^{\frac{1}{3}} |R_n - R_m|\right)$$
(2.88)

Chapter 3

Experimental

3.1 Sample preparation

CeSi_x (x = 1.80, 1.85) samples were prepared by melting together cerium (99.9% purity) and silicon (99.999% purity) in the appropriate ratios within an argon arc furnace. Each sample was remelted a minimum of five times to ensure homogeneity and then crushed and passed through a 250μ m sieve. The powder was subsequently sealed under vacuum in a quartz tube, heat treated at a temperature of 900°C for 48 hours and finally quenched into ice water. For CeSi_{1.80} a second sample was prepared by an identical preparation to that above except that this sample was slow cooled rather than quenched. Weight losses during sample preparation were less than 1% in all cases.

3.2 Magnetization measurements

Magnetization measurements have been performed on the two $\text{CeSi}_{1.80}$ and $\text{CeSi}_{1.85}$ samples using a Squid magnetometer (Kremer, 1991). The samples were placed inside gelatine capsules and measurements performed between 5K and 300K with an applied magnetic field of 0.01kOe for the $\text{CeSi}_{1.80}$ samples and 1kOe for $\text{CeSi}_{1.85}$. The corresponding temperature dependence of the inverse magnetic susceptibility is shown in Fig. 3.1. It is evident from Fig. 3.1 that the variation in the sample preparation



Figure 3.1: Inverse magnetic susceptibility of CeSi_x samples. The $\text{CeSi}_{1.80}$ (F) sample was quenched following its heat treatment whereas the $\text{CeSi}_{1.80}$ (NF) sample was slow cooled. The effective paramagnetic moment μ_{eff} is calculated from the application of the Curie-Weiss law to a linear fit of the high temperature inverse magnetic susceptibility.

(Courtesy of R.K. Kremer and M. Babateen.)



Figure 3.2: Low temperature inverse magnetic susceptibility and magnetization of CeSi_{1.80} (F), measured in an applied magnetic field of 20Oe.

(Courtesy of R.K. Kremer and M. Babateen.)



Figure 3.3: Magnetic field dependence of the magnetization of CeSi_{1.80} (F) at a temperature of 2K. (Courtesy of R.K. Kremer and M. Babateen.)

of the two CeSi_{1.80} samples has a profound effect on their magnetic ground state, the quenched sample having a ferromagnetic ground state whereas the slow cooled sample has no ordered ground state. These two samples will henceforth be referred to as CeSi_{1.80} (F) and CeSi_{1.80} (NF) in reference to their respective ferromagnetic and non-ferromagnetic ground states. Application of the Curie-Weiss law to a linear fit of the high temperature inverse magnetic susceptibility yields an effective paramagnetic moment per cerium atom of $\mu_{eff} = 2.30\mu_B$, $2.92\mu_B$ and $2.47\mu_B$ for CeSi_{1.80} (F), CeSi_{1.80} (NF) and CeSi_{1.85} respectively. The μ_{eff} of the CeSi_{1.80} (NF) sample is significantly higher than the $2.54\mu_B$ expected for a Ce³⁺ ion according to Hund's rules. However it is not abnormal in comparison with magnetization measurements made on other CeSi_x samples, § 4.2.

The low temperature inverse magnetic susceptibility of $\text{CeSi}_{1.80}$ (F) is shown in Fig. 3.2 along with the magnetization of the sample, remeasured between 2K and 15K in a magnetic field of 20Oe. The magnetic field dependence of the magnetization of $\text{CeSi}_{1.80}$ (F) at 2K is illustrated in Fig. 3.3.

3.3 Neutron powder diffraction experiments

Neutron powder diffraction experiments were performed on the $CeSi_{1.80}$ (F) and $CeSi_{1.85}$ samples between 1.5K and 300K using the diffractometers D2B and D1B at the ILL, Grenoble.

Apparatus: spectrometers D2B and D1B

A horizontal cross-sectional plan of the ILL spectrometers D2B and D1B is shown in Figures 3.4 and 3.5 respectively. D2B is a high-resolution powder diffractometer installed on a thermal neutron beam. The incident beam is reflected from a germanium monochromator with a wavelength of 1.594Å and collimated by 5' Soller collimators. The samples are contained within vanadium sample holders and placed within a standard ILL 'orange' cryostat that is operated using liquid nitrogen and liquid helium and is capable of varying the sample temperature between 1.5K and 300K. The scattered neutrons are detected by a bank of 64 ³He detectors and 5' Soller collimators, at intervals of 2.5°. The whole detector array is mounted on air pads and may be rotated about the sample. The following experiments were performed with a 2θ step of 0.05° between consecutive measurements.

D1B is a two-axis powder diffractometer with a multidetector. It is mounted on a thermal neutron guide tube and a pyrolytic graphite monochromator is used to produce an incident beam with a wavelength of 2.52Å. The sample is once again contained within a vanadium sample can and placed within an orange cryostat. The curved multidetector is filled with ³He/Xe and contains a system of multi-electrodes that divide the detector into 400 cells. The multidetector covers an angular range of $2\theta = 80^{\circ}$.

Analysis

The refinement programs used to analyse the powder diffraction patterns are based on the *Rietveld method* of structural refinement, i.e. using the method of least-squares to fit a calculated diffraction profile to the measured diffraction profile. The agreement factors that are standardly used to judge the quality of the fit are the 'weighted-profile' and 'expected' R-factors and the χ^2 value. They are defined by

$$R_{wp} = 100 \times \left[\frac{\sum_{i} w_{i} |I_{i}^{obs} - I_{i}^{calc}|}{\sum_{i} w_{i} I_{i}^{obs}}\right]$$
$$R_{exp} = 100 \times \left[\frac{N - P + C}{\sum_{i} w_{i} I_{i}^{obs}}\right]$$
$$2 \quad \left(R_{wp}\right)^{2}$$

and

$$\chi^2 = \left(\frac{R_{wp}}{R_{exp}}\right)$$

where the weights of the observations are calculated by

$$w_i = \frac{1}{\text{variance}(I_i^{obs})}$$

and (N - P + C) is the number of degrees of freedom (N is the number of points in the diffraction pattern, P the number of refined parameters and C the number of strict constraint functions). Thus R_{wp} is related to the value of the least-squares minimization function and R_{exp} is the value of R_{wp} that would be obtained if the



Figure 3.4: Horizontal cross-sectional plan of the spectrometer D2B.



Figure 3.5: Horizontal cross-sectional plan of the spectrometer D1B.

differences between the observed and calculated profiles were merely statistical in origin. In the ideal case, $\chi^2 = 1$.

Results: neutron powder diffraction refinements of D2B data for $CeSi_{1.80}$ (F) and $CeSi_{1.85}$

The PROFIL suite of refinement programs (Cockcroft, 1991) have been used to analyse the diffraction profiles measured on D2B for $\text{CeSi}_{1.80}$ (F) and $\text{CeSi}_{1.85}$. The refinements are solely for nuclear scattering from the samples; the nuclear and magnetic scattering refinements of $\text{CeSi}_{1.80}$ (F) at 1.5K and 8K have been performed using the PROF1/PROF2 refinement programs (Hewat, 1990) and will be discussed in more detail during the summary of the D1B experiment on $\text{CeSi}_{1.80}$ (F).

The best refinement for the CeSi_{1.80} (F) sample was obtained at all temperatures by the space group *Imma*, i.e. the GdSi₂-type structure. Attempts to refine the diffraction data with the space group $I4_1/amd$ (ThSi₂-type structure) were unsuccessful in accounting for the observed peak splitting at high 2θ . The variation of the lattice parameters and unit cell volume as a function of temperature are shown in Fig. 3.6 where the estimated standard deviations in the lattice parameters are smaller than the markers used to illustrate them, e.g. at 1.5K, a=4.1627(2)Å, b=4.1551(2)Å and c=13.8370(4)Å. The nuclear refinement at 15K is shown in Fig. 3.7. There is no evidence either for the coexistence of two phases in this sample or for the presence of a silicon impurity phase.

Within the error of the refinement there is no significant variation in the cerium or silicon z-parameters with temperature; $z_{Ce} = 0.3771(4)$, 0.3772(8), $z_{Si_1} = 0.7877(4)$, 0.7910(7) and $z_{Si_2} = 0.9560(4)$, 0.9588(8) at 1.5K and 300K respectively. The cerium atoms were refined with isotropic temperature factors. However, an improvement in the refinement was observed with the inclusion of anisotropic temperature factors for the silicon atoms. Tables 3.1 and 3.2 list the refined lattice site occupations and temperature factors as a function of temperature. The cerium lattice site occupation was held fixed at 1.00 throughout.

A review of the anisotropic temperature factors shows that for the silicon deficient



Figure 3.6: Temperature dependence of the lattice parameters and unit cell volume of CeSi_{1.80} (F); \diamond represents the results of the neutron refinements (ILL) and for comparison **m** denotes the X-ray synchrotron refinements (SRS). For the bottom figure $\diamond = a, \diamond = b$, **m** = a and **m** = b.



Figure 3.7: Neutron powder diffraction refinement of $\text{CeSi}_{1.80}$ (F) at 15K. The upper line illustrates the experimentally observed neutron counts (dots) and the calculated fit to the observed diffraction profile (solid line). The markers indicate the positions of the nuclear Bragg peaks for the refinement. The lower line illustrates the difference between the observed and calculated diffraction profiles.

Table 3.1: Silicon lattice site occupations and refinement R-factors for the nuclear scattering refinements of CeSi_{1.80} (F).

T (K)	Occupation	Occupation	R _{wp}	Rexp	χ^2
	Si_1	Si ₂			
1.5	0.85(2)	1.05(2)	14.3	4.4	10.6
8	0.83(2)	1.04(2)	14.4	4.3	11.2
15	0.83(2)	1.03(2)	14.1	4.3	10.8
100	0.83(3)	1.05(3)	15.0	4.3	12.2
150	0.83(3)	1.03(3)	15.4	4.4	12.3
200	0.82(3)	1.05(3)	15.2	4.5	11.4
250	0.80(3)	1.05(3)	15.9	4.7	11.4
300	0.82(4)	1.00(4)	17.7	6.0	8.7

Si₁ lattice site the B₂₂ and B₃₃ parameters are consistently refined to be approximately zero. The significant thermal motion of the silicon atoms is occurring along the *a*-axis, the longer of the two axes defining the basal plane. At all temperatures the thermal motion ellipsoid of the Si₂ lattice site is enhanced in the basal *a-b* plane compared to that along the crystallographic *c*-axis. The 1.5K nuclear and magnetic scattering refinement of CeSi_{1.80} (F) gives an ordered moment of $0.45(6)\mu_B$ per cerium atom. Such a magnetic moment is consistent with the observations on other magnetically ordered CeSi_x ($x \leq 1.80$) samples (§ 4.3), yet smaller than the moment of $1.07\mu_B$ per cerium atom expected for the ground state doublet of the crystalline electric-field split $J = \frac{5}{2}$ multiplet.

The refinement of D2B data for $\text{CeSi}_{1.85}$ reveals a significant difference in the crystallographic structure of this sample compared to that of $\text{CeSi}_{1.80}$ (F). At all temperatures (1.5K \rightarrow 300K) it is not possible to refine the data with only one phase of the ThSi₂-type (space group $I4_1/amd$) or GdSi₂-type (space group Imma) structures. Such single phase refinements are not sufficient to account for the peak splitting observed at high 2θ , as illustrated in Fig. 3.8. For temperatures $T \leq 200$ K the two phase refinements consistently refine a silicon 'rich' ($x \approx 2.0$) and silicon 'poor' ($x \approx 1.8$) CeSi_x phase. The refinements are marginally improved if the 'rich'



Figure 3.8: Single phase and two phase refinements of high angle D2B data for CeSi_{1.85} at 300K. The difference line (i.e. the difference between the observed and calculated diffraction intensities) is significantly improved for the two phase refinement compared to that of the single phase refinements.

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T (K)	Lattice site	B_{11}^{Si}	B^{Si}_{22}	${ m B}_{33}^{Si}$	B ^{Ce} iso
1.5	Si1	0.024(5)	0.001(3)	0.0006(4)	`0.08(7)
	Si ₂	0.010(3)	0.009(3)	0.0012(3)	
8	Si_1	0.022(5)	0.001(3)	0.0004(5)	0.15(7)
	Si_2	0.009(3)	0.009(4)	0.0013(4)	
15	Si_1	0.020(5)	0.001(3)	0.0002(5)	0.12(7)
	Si_2	0.006(3)	0.013(4)	0.0014(4)	
100	Si_1	0.018(6)	0.007(4)	0.0000(6)	0.17(8)
	Si_2	0.007(3)	0.014(5)	0.0018(5)	
150	Si_1	0.017(6)	0.011(5)	0.0000(7)	0.25(8)
	Si_2	0.005(4)	0.013(5)	0.0018(7)	
200	Si1	0.029(6)	0.010(5)	0.0002(7)	0.33(8)
	Si_2	0.006 (4)	0.008(4)	0.0017(7)	
250	Si_1	0.023(6)	0.011(5)	0.0001(9)	0.46(9)
	Si_2	0.006(3)	0.011(5)	0.0019(7)	
300	Siı	0.030(8)	0.006(5)	0.0000(6)	0.5(1)
	Si ₂	0.014(5)	0.006(6)	0.0035(8)	

Table 3.2: Refined temperature parameters for CeSi_{1.80} (F).

and 'poor' phases have the space groups $I4_1/amd$ and Imma respectively, rather than both phases being refined with $I4_1/amd$ or Imma. Thus these refinements indicate that, as described in § 1.1, the crystal structures of the two phases differ by the presence of a small distortion of the a and b axes within the silicon 'poor' phase such that the tetragonal a = b condition is no longer satisfied. The silicon 'rich' phase is tetragonal. For $T \ge 225$ K, due to the proximity in the lattice parameters of the two phases, it was found more reasonable to refine both phases with the tetragonal space group $I4_1/amd$. This reduced the number of refinement codewords required for the refinement and enabled a realistic refinement of the anisotropic temperature factors for the silicon atoms. However, an orthorhombic distortion in one of the two phases between 225K and 300K cannot be ruled out within the accuracy of these refinements. There is no clear evidence of a silicon impurity phase in the sample. For $T \ge 250$ K the refinements suggest a silicon 'rich' and 'poor' phase in the sample but it is not certain as to which phase is associated with the greater silicon concentration or which phase is present in the greater proportion. The R-factors for the refinement remain the same when the silicon concentrations of the 'rich' and 'poor' phases are inverted, and also when the relative proportions of the two phases are inverted. For this reason the refined lattice parameters shown in Fig. 3.9 are not assigned to a silicon 'rich' or 'poor' phase for $T \ge 250$ K. It should be noted, however, that the estimated standard deviations in the lattice parameters are still smaller than the markers used to illustrate them.

The refined powder diffraction profile for the $\text{CeSi}_{1.85}$ sample at 1.5K is illustrated in Fig. 3.10. As with the refinements of $\text{CeSi}_{1.80}$ (F), there is no significant temperature variation of the cerium or silicon z-parameters within the accuracy of the refinement. For the silicon 'rich' phase $z_{Si} = 0.2907(2)$, 0.2913(4) at 1.5K and 300K respectively. For the silicon 'poor' phase $z_{Ce} = 0.3782(5)$, 0.378(1), $z_{Si_1} = 0.7887(6)$, 0.7917(9) and $z_{Si_2} = 0.9566(5)$, 0.9593(8) at 1.5K and 200K. The temperature variation of the silicon lattice site occupations for the two phases are shown in Table 3.3 along with the R-factors for the refinement. Again the cerium lattice site occupation was fixed at 1.00 for both phases. The increase in the R-factors above 200K are indicative of the increase in the uncertainty of the two phase refinement due to the very small peak splitting observed in the diffraction profile at these temperatures.

The refined temperature factors for the silicon 'poor' phase in the CeSi_{1.85} sample are very similar to those listed in Table 3.2 for CeSi_{1.80} (F). Between 1.5K and 200K where the resolution of the two phases is most accurate, the silicon deficient Si₁ site has $B_{11} \approx 0.020(5)$ whereas B_{22} and B_{33} are consistently refined to be zero. The Si₂ site again has a larger thermal motion ellipsoid in the *a-b* plane compared to that along the *c*-axis. For the tetragonal silicon 'rich' phase $B_{11} \approx 0.014(1)$ between 1.5K and 200K whereas $B_{33} \approx 0.0014(2)$.

Expressing the low temperature phase separation within the CeSi_{1.85} sample by

$$\operatorname{CeSi}_{1.85} \longrightarrow \eta \operatorname{CeSi}_{y} + (1 - \eta) \operatorname{CeSi}_{z}$$
 (3.1)

where y < z such that CeSi_y represents the silicon 'poor' phase and CeSi_z the silicon 'rich' phase, the neutron powder diffraction refinements of $\text{CeSi}_{1.85}$ give a temperature





Figure 3.9: Temperature dependence of the lattice parameters and unit cell volume of CeSi_{1.85}; a) from the neutron refinements (ILL), b) from the X-ray synchrotron refinements (SRS). In both figures \blacktriangle denotes the tetragonal phase, \diamond the orthorhombic and in the bottom figures the *a* and *b* lattice parameters of the orthorhombic phase are distinguished by $\diamond = a$ and $\diamond = b$. For the neutron refinements (ILL) at $T \ge 250$ K where it is not possible to distinguish the silicon concentrations of the phases, the points are marked by \diamond .





T (K)	Occupation	Occupation	Rwp	Rexp	χ^2
	(silicon 'rich' phase)	(silicon 'poor' phase)			
	Si ₁	Si ₁ & Si ₂			
1.5	2.17(8)	0.83(3) & 1.00(4)	12.6	4.5	7.8
100	2.25(9)	0.80(3) & 0.99(4)	12.3	4.5	7.5
150	2.13(9)	0.85(4) & 1.01(4)	12.9	4.5	8.2
175	2.08(9)	0.84(4) & 1.02(5)	13.0	4.5	8.3
200	2.03(9)	0.84(7) & 1.00(8)	13.7	4.3	10.1
225	2.01(9)	1.8(2)	13.7	4.2	10.6
250	2.00(5)	1.7(3)	16.0	4.2	14.5
275	2.1(2)	1.9(1)	12.9	4.2	9.4
300	2.0(2)	1.9(1)	12.0	4.1	8.6

Table 3.3: Silicon lattice site occupations and refinement R-factors for CeSi_{1.65}.



Figure 3.11: Temperature dependence of η , the fraction of the silicon 'poor' phase coexisting in the CeSi_{1.85} sample. Within the uncertainty of the refinement, for $T \ge 250$ K the two possibilities for η are given.

dependence of η as shown in Fig. 3.11.

Results: neutron powder diffraction refinements of D1B data for $CeSi_{1.80}$ (F)

Measurements have been performed on $\text{CeSi}_{1.80}$ (F) at 1.3K, 9.4K, 12.4K and 15.0K. Diffraction patterns illustrating the low temperature magnetic scattering contribution to the diffraction profile are shown in Fig. 3.12. There is no evidence here for magnetic reflections with a magnetic propagation vector $q_m \neq 0$. Within the statistics of these measurements it is not possible to discuss the existence/non-existence of an antiferromagnetic modulation of the magnetic scattering intensity at $q_m = 0$. Such a modulation has previously been observed to be superposed onto the ferromagnetic scattering intensity of a single crystal of $\text{CeSi}_{1.70}$ (Sato *et al.*, 1985). The best nuclear and magnetic refinements of the diffraction profile at 1.3K are obtained for an ordered magnetic moment of $0.5(1)\mu_B$ in the basal *a-b* plane.

3.4 X-ray synchrotron powder diffraction experiments

High resolution X-ray synchrotron diffraction experiments were performed on the CeSi_{1.80} (F), CeSi_{1.80} (NF) and CeSi_{1.85} samples using station 2.3 on the Synchrotron Radiation Source (SRS) at Daresbury Laboratory, England. The aim of these experiments was to investigate the nature of the structural instability observed in CeSi_x by neutron powder diffraction, in more detail.

Apparatus: station 2.3

The high resolution powder diffractometer at station 2.3 is equipped with a helium cryostat, enabling measurements to be performed between sample temperatures of 10K and 300K. The incident radiation is monochromated by a Ge(111) monochro-



Figure 3.12: Difference patterns from D1B data for $\text{CeSi}_{1.80}$ (F). The patterns illustrate the difference between the scattered neutron intensity at two different sample temperatures. The positions of the nuclear Bragg reflections at 1.3K are indicated for the (1.3K)-(15.0K) subtraction data.

mator and measurement of a NBS silicon standard gave the incident wavelength as 1.39760Å. The samples were compacted onto a rotating flat plate copper sample holder. The sample volume had a diameter of 2.5cm and a depth of 0.2cm. An 8μ m layer of polyamide ('mylar') was used to cover the sample and minimize any movement of the sample surface during rotation. The following measurements were made using a count time of 1 second at each detector position and a 2θ step of 0.01° between successive detector positions.

Results and analysis

The CeSi_{1.80} (F) sample was measured at 291K, CeSi_{1.80} (NF) at 10K, 100K, 200K and 293K, and CeSi_{1.85} at temperatures of 10K, 200K and 280K. The MPREP/MPROF multipattern Rietveld refinement programs (Fitch *et al.*, 1993) were used for the analysis of the diffraction profiles. Early attempts to analyse the data via the Rietveld method illustrated that such refinements were not possible due to the 'coarseness' of the sample. An example of the problem is shown in Fig. 3.13 where the observed and calculated diffraction profiles for CeSi_{1.80} (F) at 291K are illustrated. The reflection shown was indexed as the (112) reflection of the space group *Imma*. The asymmetrical shape and jaggedness of the peak is attributed to the presence of large crystallites within the powder sample that are scattering preferentially and destroying the powder averaging. Attempts to perform a Rietveld refinement of the atomic site occupations, temperature factors or half-width parameters for this diffraction profile yielded unphysical results. The 2θ step of 0.01° between successive detector positions may clearly be observed in Fig. 3.13a.

A similar 'jaggedness' of the peak shapes was observed for all three of the CeSi_x samples measured on station 2.3. Thus, with hindsight, it is clear that an upper crystallite size of 250μ m is too large for such high-resolution experiments. To perform a physical refinement of the observed diffraction profiles, a *cell-constrained profile fitting* method was employed rather than the Rietveld method. This method (available within MPROF version X15.6) uses the procedure of Le Bail (1988) and refines a calculated profile as in the Rietveld method, except that the integrated intensities are not given by a structural model but are variables in the least-squares refinement.





Figure 3.13: The (112) reflection from $\text{CeSi}_{1.80}$ (F) at 291K; a) the observed profile, b) the observed (dotted) and calculated (solid line) profile using the cell-constrained method.



Figure 3.14: Temperature dependence of the lattice parameters of $\text{CeSi}_{1.80}$ (NF). \blacktriangle denotes the tetragonal phase and \blacklozenge the orthorhombic phase. For the bottom figure $\blacklozenge = a$ and $\diamondsuit = b$.



Figure 3.15: The refined diffraction profiles of $\text{CeSi}_{1.80}$ (NF) at 10K and 100K using the cell-constrained method. The (116) and (11 10) reflections indexed by the tetragonal phase are labelled [T]. The corresponding reflections from the orthorhombic phase are labelled [O].

The procedure allows the zero-offset and lattice parameters to be accurately refined but yields no information regarding the peak shapes and integrated intensities. This method has been used for all of the refinements described below.

The refined lattice parameters for $\text{CeSi}_{1.80}$ (F) at 291K have been included in Fig. 3.6 to allow an easy comparison with the neutron diffraction measurements. As with the neutron refinement, all observed reflections are well accounted for by a single phase with the space group *Imma* (i.e. the GdSi_2 -type structure).

The temperature dependence of the lattice parameters of $\text{CeSi}_{1.80}$ (NF) is shown in Fig. 3.14. Once again, the estimated standard deviations in the refined lattice parameters are smaller than the markers used to illustrate them, e.g. at 10K the lattice parameters of the orthorhombic phase are refined to be $a=4.1599\text{\AA}$, $b=4.1545(1)\text{\AA}$ and $c=13.8448(2)\text{\AA}$. The existence of two phases in the sample at 10K and 100K may clearly be seen from the refined diffraction profiles of Fig. 3.15. The initial refinements at these temperatures were performed by the cell-constrained method for two orthorhombic phases with the space group Imma. However, the *a* and *b* parameters for one of the phases were consistently refined to be approximately equal and a refinement with one tetragonal phase (space group $I4_1/amd$) and one orthorhombic phase (space group Imma) proved totally adequate to account for all of the observed reflections. At 200K and 293K there is no conclusive evidence for the existence of a second phase. A single phase Imma is sufficient to index all of the observed reflections at these temperatures. It is remarked, however, that for such a single phase refinement, the orthorhombic distortion of the *a* and *b* lattice parameters is very small. From Fig. 3.15 it may also be observed that the proportion of the two phases remains approximately constant between 10K and 100K.

The diffraction profiles from $\text{CeSi}_{1.85}$ are illustrated in Fig. 3.16 and clearly show the existence of two phases within the sample at all temperatures measured; 10K, 200K and 280K. They also confirm that the relative proportions of the two phases are temperature dependent. The refinements were performed using one tetragonal phase with the space group $I4_1/amd$ and a second orthorhombic *Imma* phase. It was tested whether the refinement would be improved if the profile was fitted by two orthorhombic phases but this was not the case; the *a* and *b* lattice parameters of one phase consistently being refined to be equal. As for the possibility of two tetragonal $I4_1/amd$ phases in the sample at 280K, these experiments clearly show that this is not the case.

The temperature dependence of the lattice parameters of $\text{CeSi}_{1.85}$ have been illustrated in Fig. 3.9b in order to allow an easy comparison with the results of the neutron diffraction experiments. Such a comparison shows that the lattice parameters from the two diffraction experiments are in very good agreement, both in magnitude and temperature dependence. The SRS experiment confirms that at a temperature of 280K the two phases coexisting with the $\text{CeSi}_{1.85}$ sample do have different crystallographic structures, one being the tetragonal ThSi₂-type structure and the other being the orthorhombic GdSi₂-type structure. Though both experiments show that the relative proportion of the tetragonal and orthorhombic phases coexisting within the sample is temperature dependent, at low temperatures the SRS experiment has a greater proportion of the tetragonal phase whereas the neutron experiment has a greater proportion of the orthorhombic phase.



Figure 3.16: The refined diffraction profiles of $\text{CeSi}_{1.85}$ at 10K, 200K and 280K using the cell-constrained method. The (116) and (11 10) reflections indexed by the tetragonal phase are labelled [T]. The corresponding reflections from the orthorhombic phase are labelled [O].

3.5 Electron microscopy

The CeSi_{1.80} (NF) and CeSi_{1.85} samples have been examined at room temperature using a scanning electron microscope equipped with an energy-dispersive X-ray detector (Bates & Zayer, 1993). The powder samples were remelted, mounted in a conducting bakelite block and their surfaces polished and cleaned. An incident electron beam of 20keV was used for the analysis. The backscattered electron images were recorded on polaroid film and the emitted X-rays were analyzed spectroscopically. Figures 3.17 and 3.18 show the backscattered electron images for CeSi_{1.80} (NF) and CeSi_{1.85} respectively. The intensity of electron backscattering is proportional to the concentration of scattering atoms and their atomic number (Z); a single atom with a large Z giving a relatively light image compared to that from a single atom with a small Z.

In Fig. 3.17b the crystalline nature of $\text{CeSi}_{1.80}$ (NF) may be observed. The light areas are large crystals of CeSi_x and are surrounded by a small amount of pure silicon (dark area). Analysis of the emitted X-rays from various light areas in the image gave the same relative proportion of cerium and silicon atoms, thus supporting the single phase nature of $\text{CeSi}_{1.80}$ (NF) at room temperature. It was not possible to measure a cerium standard during this experiment and as such, the concentrations can not be placed on an absolute scale.

In Fig. 3.18b the very dark particle (marked with a white cross) is pure silicon, proving the existence of a small silicon impurity phase in CeSi_{1.85}. Elsewhere in this image there are grey regions with different contrasts. Spectroscopic analysis of the Xrays emitted from these regions prove that they contain different relative proportions of cerium and silicon atoms. These observations support the coexistence of two phases CeSi_y and CeSi_z ($y \neq z$) within CeSi_{1.85} at room temperature.

3.6 Paramagnetic scattering experiments

The paramagnetic scattering from $\text{CeSi}_{1.80}$ (F), $\text{CeSi}_{1.80}$ (NF) and $\text{CeSi}_{1.85}$ powder samples has been investigated on the spectrometer D7 at the Institut Laue-Langevin, Grenoble. Spin polarized neutrons and spin polarization analysis have been used



a)



b)

Figure 3.17: Backscattered electron images from SEM analysis of $\text{CeSi}_{1.80}$ (NF) at room temperature; a) ×200 magnification, b) ×1460 magnification. In b) the light areas are CeSi_{x} and are surrounded by a small amount of pure silicon.

(Courtesy of J. Bates and N.K. Zayer.)



a)



b)

Figure 3.18: Backscattered electron images from SEM analysis of $CeSi_{1.85}$ at room temperature; a) $\times 200$ magnification, b) $\times 1170$ magnification. In b) the white cross marks the area analyzed to be pure silicon. (Courtesy of J. Bates and N.K. Zayer.)
to unambiguously separate the magnetic diffuse scattering from all other scattering contributions.

Apparatus: the spectrometer D7

The instrument D7 is a multi-purpose spectrometer that may be operated in a *time-of-flight* or *integral* mode and with or without 3-dimensional polarization analysis. A detailed description of the apparatus, calibration measurements and the theory of x - y - z polarization analysis have been given by Schärpf (1985) and Schärpf & Capellmann (1993). However, for completeness, an overview of the essential components and operation of the spectrometer are described here.

A perspective view and a horizontal cross-section of D7 are shown in Fig. 3.19 and Fig. 3.20. The spectrometer is a 'two axis' instrument with 64 detectors mounted in a horizontal plane (labelled x - y) together with the incident beam. The axis of quantization, i.e. the axis along which the neutron spins are polarized and analyzed, is the z-axis.

Following the path of the neutron beam through the spectrometer, the incident neutrons may be selected from three orientations of the triple graphite monochromator with a wavelength of 3.1Å, 4.8Å or 5.7Å. The supermirror polarizer (described briefly below) only transmits neutrons of one spin state, in this case neutron spins in a 'spin up' state along the z-axis, and combined with the beryllium filter supresses higher order monochromator reflections. The neutron spin may subsequently be reversed to the 'spin down' state by the flipper which consists of a Mezei coil with a horizontal (x - y) field direction and a second coil wound directly onto this coil but with a magnetic field in the vertical (z) direction. The latter is required so that a vertical guide field is maintained outside the flipper to avoid depolarization of the polarized beam (Schärpf, 1980). A mechanical chopper provides the possibility of time-of-flight analysis of the diffracted beam but in the experiments described here this was not present. Thus the spectrometer was operated in 'integral' mode with each detector measuring scattering events and integrating over all energy transfers.

The sample is contained within a aluminium sample can and placed inside a



Figure 3.19: The spectrometer D7.



Figure 3.20: Horizontal cross-sectional plan of D7.



Figure 3.21: Supermirror polarizers mounted in a magnetic field, courtesy of Schärpf (1989b).

variable temperature, type 'orange' ILL cryostat, adapted for neutron scattering experiments. Three orthogonal coil pairs surround the sample and enable the guide field of approximately 20Oe at the sample to be aligned along the x, y or z-axes. The scattered neutrons are observed using 64 ³He detectors, 32 of which are equipped with supermirror analyzers that may be inserted or removed by pneumatic elevators, enabling experiments to be performed with or without spin polarization analysis.

The neutron spin polarization and polarization analysis are achieved by supermirror polarizers (Schärpf, 1989a, 1989b). The supermirrors are coated with layers of cobalt and a contrast material for one spin, matched so the the wrong spin does not see a contrast. They are arranged so as to form the walls of a collimator and are surrounded by strong permanent magnets that define the direction of the field, Fig. 3.21. The polarizer works by virtue of there being a magnetic contribution to the neutron refraction index such that there are different refraction indices for different spin alignments of the neutrons. The curvature of the supermirror collimator is chosen such that no neutron can traverse the collimator without being at least once reflected by the magnetized cobalt wall or absorbed.

Calibration measurements required for determination of the paramagnetic cross section via spin polarization analysis

The scattered neutron intensity measured by each detector consists of the sample signal and a background signal i.e. the neutrons scattered from the sample holder, cryostat, etc. ..., and air scattering. The background signal has two contributions, one absorption dependent and the other absorption independent. The former is that part of the environment scattering that occurs after the beam has traversed the sample, illustrated as region A in Fig. 3.22, and is dependent on the transmission of the sample. To determine the correct background signal (I_b) that must be subtracted from the measured signal, a measurement of the empty sample holder (I_e) is not sufficient. A measurement I_{Cd} is also required in which the sample is replaced by cadmium with a large neutron absorption cross section. The corrected background signal is then given by

$$I_b = I_{Cd} + T_{m_e} \left(I_e - I_{Cd} \right) \tag{3.2}$$

where T_{m_x} , the transmission of sample x, is determined from

$$T_{m_x} = \frac{I'_x - I'_{Cd}}{I'_e - I'_{Cd}}$$
(3.3)

Within (3.3) $I' = \frac{I(mon(2))}{I(mon(1))}$, i.e. the ratio of the neutron counts recorded by monitors (2) and (1) whose respective positions in the direct beam are after and before the sample, as illustrated in Fig. 3.20.

For the first measurement and all subsequent measurements using a different incident wavelength, the currents applied to the x, y and z spin-turner coils are 5A and the current in the flipper and correction coils are adjusted in order to achieve the optimum flipping ratio. The finite flipping ratio at each detector position is then determined via a quartz measurement. Amorphous quartz (Si+O) is used for this purpose. It is a glass and so has no Bragg peaks and only coherent diffuse nuclear scattering. It also has no nuclear spin, thus its scattering cross section has only diffuse non-spin flip contributions. A measurement of the non-spin flip and spin flip scattering of amorphous quartz for all three polarization directions thus yields the fraction of the neutron-spins of the 'wrong' spin state that have traversed the apparatus in each case.



Figure 3.22: Contibutions to the background intensity due to 'environment' scattering for a) the sample, b) cadmium and c) an empty sample holder.

The experimental correction for the relative efficiencies of the detectors for elastic scattering is obtained via a vanadium measurement. Vanadium has a very small coherent and a large incoherent scattering cross section (0.0184 and 5.187 barn respectively) and thus its scattering is effectively isotropic. For such a measurement, the differences in the neutron counts recorded by each detector yields their relative efficiency. Corrections are also performed for the sample absorption, the scattering vector dependence of the cerium form-factor (Forsyth & Wells, 1959; Brown, 1992) and for multiple scattering from the sample. The latter is done using a Monte-Carlo simulation program (Schärpf, 1990). Finally, by relating the observed vanadium scattering to the weight of the vanadium sample, the vanadium measurement is used once again to place the experimental cross sections onto an absolute scale. The normalization is performed by

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{\sigma_{inc}^{van}}{4\pi} \left(\frac{n^{van}}{n^x}\right) \frac{I_{exp}^x}{I_{exp}^{van}}$$
(3.4)

where σ_{inc}^{van} is the vanadium incoherent scattering cross section, n^{van} and n^{x} are the number of respective nuclei in the samples, (I_{exp}^{van}) and (I_{exp}^{x}) are the vanadium and sample measurements that have previously undergone all of the corrections described above.

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Results

Experiments have been performed on the $\text{CeSi}_{1.80}$ (F), $\text{CeSi}_{1.80}$ (NF) and $\text{CeSi}_{1.85}$ powder samples between 1.5K and 300K with the spectrometer D7 in 'integral' mode and with 3-dimensional spin polarization analysis. An incident wavelength of 4.8Å (3.5 meV) and 5.7Å (2.5 meV) were used for the measurements on $\text{CeSi}_{1.80}$ and $\text{CeSi}_{1.85}$ samples, respectively. The observed spin flip (sf) and non-spin flip (nsf) scattering intensities for the incident neutron spin polarization along the x, y and z-axis have been corrected for background scattering, relative detector efficiencies, finite flipping ratios, absorption, multiple scattering and the cerium form-factor dependence, as described above. The paramagnetic differential scattering cross section has been calculated, independently of any model assumptions, from the combinations of the measured cross sections shown in equations (2.59) and (2.60), i.e.

$$\left(\frac{d\sigma_{para}}{d\Omega}\right)^{sf} = 2\left[\left(\frac{d\sigma}{d\Omega}\right)_{x}^{sf} + \left(\frac{d\sigma}{d\Omega}\right)_{y}^{sf} - 2\left(\frac{d\sigma}{d\Omega}\right)_{z}^{sf}\right]$$

and

$$\left(\frac{d\sigma_{para}}{d\Omega}\right)^{nsf} = 2\left[2\left(\frac{d\sigma}{d\Omega}\right)_{z}^{nsf} - \left(\frac{d\sigma}{d\Omega}\right)_{x}^{nsf} - \left(\frac{d\sigma}{d\Omega}\right)_{y}^{nsf}\right]$$

The paramagnetic differential scattering cross section given by

$$\left(\frac{d\sigma_{para}}{d\Omega}\right) = \frac{1}{2} \left[\left(\frac{d\sigma_{para}}{d\Omega}\right)^{sf} + \left(\frac{d\sigma_{para}}{d\Omega}\right)^{nsf} \right]$$
(3.5)

i.e. the average of $\left(\frac{d\sigma_{para}}{d\Omega}\right)$ determined from measurements of the spin flip and nonspin flip scattering, is illustrated for each of the three samples in Figures 3.23 and 3.24 as a function of temperature and the scattering vector, κ .

The corrected coherent and incoherent scattering contributions from each of the three samples are illustrated in Figures 3.25 and 3.26. The latter measurement may be used as a check of the corrections applied to the raw data. As expected, the cross sections are κ independent. The CeSi_{1.80} (F) and (NF) measurements have been corrected using exactly the same set of calibration measurements. Though the CeSi_{1.80} (F) measurement was performed at a temperature only marginally above the ferromagnetic ordering temperature ($T_c = 12.5$ K), the neutron spin flipping ratios indicate no depolarization of the beam at this temperature due to the onset of magnetic order within the sample. The small variation in the magnitude of σ_{inc} for CeSi_{1.80} (F)



Figure 3.23: Temperature and scattering vector dependence of the differential paramagnetic cross section of $\text{CeSi}_{1.80}$ (F) and $\text{CeSi}_{1.80}$ (NF). The data points \blacksquare at zero scattering vector represent the differential paramagnetic scattering cross section calculated from measurement of the magnetic susceptibility of the samples.



Figure 3.24: Temperature and scattering vector dependence of the differential paramagnetic cross section of $\text{CeSi}_{1.85}$. The data points \blacksquare at zero scattering vector represent the paramagnetic differential scattering cross section calculated from measurement of the magnetic susceptibility of the sample.



Figure 3.25: Low temperature coherent differential scattering cross section.



Figure 3.26: Low temperature incoherent differential scattering cross section.



Figure 3.27: The differential paramagnetic scattering cross section of CeSi_{1.85} at 150K. The positions of the nuclear Bragg reflections are indicated by the open arrows.

and (NF) could be the result of a small amount of water contamination in the former sample.

From Fig. 3.23 it is evident that ferromagnetic correlations are present in CeSi_{1.80} (F) at 13K. In contrast, the paramagnetic differential scattering cross section of CeSi_{1.80} (NF) has no correlations whatsoever at low temperatures. For the latter the magnetic scattering is κ independent, resembling the behaviour of a perfect paramagnet. Fig. 3.23 also illustrates a striking difference between the magnitudes of the $\left(\frac{d\sigma_{para}}{d\Omega}\right)$ of the two CeSi_{1.80} (NF) at factor of six difference between $\left(\frac{d\sigma_{para}}{d\Omega}\right)$ of CeSi_{1.80} (F) at 13K and that of CeSi_{1.80} (NF) at 1.5K.

The paramagnetic differential scattering cross section of CeSi_{1.85} is shown in Fig. 3.24. At 1.5K it is κ independent, similar to that observed for CeSi_{1.80} (NF). However, the temperature dependence of $\left(\frac{d\sigma_{para}}{d\Omega}\right)$ of CeSi_{1.85} is surprisingly different from that of the CeSi_{1.80} (NF) sample. Magnetic correlations are observed at higher temperatures, the magnitude of which increase with increasing temperature. Fig. 3.27 shows an enlargement of the $\left(\frac{d\sigma_{para}}{d\Omega}\right)$ of CeSi_{1.85} at 150K with the inclusion of arrows to illustrate the corresponding positions of the nuclear Bragg reflections. The enhancement of the magnetic scattering is observed at scattering vectors away from the positions of the nuclear Bragg reflections, thus indicating the existence of antiferromagnetic correlations in CeSi_{1.85}.

As discussed in § 2.1, in the limit $\kappa \to 0$ the paramagnetic differential scattering cross section may be calculated from measurement of the bulk magnetic susceptibility of the sample. Such calculations have been performed using the measurements described in § 3.2 and the results are included within Figures 3.23 and 3.24. They are in good agreement with the paramagnetic differential cross sections measured on D7. A comparison of the temperature dependence of the paramagnetic cross sections observed on D7 with those expected taking into consideration the effect of the crystalline electric-field within these samples is discussed in detail below.

Comparison of the experimental and theoretical temperature dependence of σ_{para} due to the crystalline electric-field

In a solid the 4f electron of a Ce³⁺ ion experiences perturbations from the surrounding ions, the two most important of which are due to the crystalline electric-field and magnetic interactions as discussed in § 1.2 and § 2.3. The effects of such perturbations will be observed in the magnitude and temperature dependence of the paramagnetic scattering cross section, σ_{para} . The following discussion considers the effect of the crystalline electric-field (CEF).

The CEF experienced by an ion in a lattice is the result of the Coulomb electrostatic potential of the neighbouring charge distribution and as such reflects the symmetry of the surroundings of the ion. In the following analysis a point charge model is used to determine the total electrostatic potential experienced by a reference ion due to its neighbouring ions. The Hamiltonian for the CEF, conventionally expressed in terms of the Stevens' 'operator equivalents' O_i^m (Stevens, 1952), is given by

$$\mathcal{H}_{CEF} = \sum_{l,m} B_l^m O_l^m \tag{3.6}$$

The B_i^m are the CEF parameters that are measured experimentally and a complete list of the O_i^m have been tabulated by Hutchings (1964).

For rare-earth ions the radius (r) of the 4f shell is small and the energy of the

crystalline electric-field is expected to be small since it is a function of $\langle r^2 \rangle$. The energy of the CEF interaction is generally an order of magnitude smaller (typically 0.01 meV) than that of the spin-orbit coupling (0.1 eV) and thus the following discussion may be restricted to the CEF splitting of the (2J + 1) ground state multiplet. For the tetragonal point symmetry D_{2d} of Ce³⁺ in tetragonal CeSi_x (ThSi₂-type structure), the corresponding CEF Hamiltonian is

$$\mathcal{H}_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 \tag{3.7}$$

with the crystallographic c-axis taken as the z-axis. Kramer's degeneracy restricts the splitting of the $J = \frac{5}{2}$ multiplet into three doublets within the CEF. Using the matrix representation of the Stevens' operators that have been tabulated by Hutchings (1964), then for a Ce³⁺ ion in the potential (3.7) the matrix representations of the O_i^m are

$$O_{2}^{0} = 2 \begin{pmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 5 \end{pmatrix}, O_{4}^{0} = 60 \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{5} & 0 & 0 & 0 & 0 \end{pmatrix}$$
(3.8)

and

According to Birgeneau (1972), for a given J-multiplet and for the limit of small neutron momentum transfers the partial differential magnetic scattering cross section for a system of N non-interacting ions is given by

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = N \left(\frac{1.91 e^2}{2mc^2} \right)^2 g_J^2 |f(\kappa)|^2 \frac{k_f(\omega)}{k_i} \sum_{n,m} \rho_n |\langle n|\hat{J}_\perp|m\rangle|^2 \delta\left(E_n - E_m - \omega\right)$$
(3.9)

where \hat{J}_{\perp} is the component of the total angular momentum operator perpendicular to the scattering vector κ , $|n\rangle$ and $|m\rangle$ are the eigenstates belonging to a given J-multiplet, g_J is the Landé splitting factor and $f(\kappa)$ represents the magnetic formfactor. Equation (3.9) is known as the 'dipole approximation'. For a powder sample it can be shown (Schärpf *et al.*, 1992) that the powder averaging results in

$$|\langle n|\hat{J}_{\perp}|m\rangle|^{2} = \frac{2}{3} \left[|\langle n|\hat{J}_{z}|m\rangle|^{2} + |\langle n|\hat{J}_{z}|m\rangle|^{2} + |\langle n|\hat{J}_{y}|m\rangle|^{2} \right]$$
(3.10)

To determine the transition probabilities $|\langle n|\hat{J}_{\alpha}|m\rangle|^2$ ($\alpha = x, y, z$) the eigenvalues E_m and eigenvectors $|m\rangle$ of the crystalline electric-field Hamiltonian (3.7) are required. These have been determined using a suitable computer program (Schärpf, 1991) that diagonalizes \mathcal{H}_{CEF} . By writing the (2J+1) possible eigenfunctions of the spin angular momentum operator \hat{J}_{α} ($\alpha = x, y, z$) in matrix form, i.e. for $J = \frac{5}{2}$,

$$\begin{split} \sum_{n,m} \langle n | \hat{J}_x | m \rangle \Rightarrow \frac{1}{2} \begin{pmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & -5 \end{pmatrix} \\ \sum_{n,m} \langle n | \hat{J}_x | m \rangle \Rightarrow \frac{1}{2} \begin{pmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & 2\sqrt{2} & 0 & 3 & 0 & 0 \\ 0 & 0 & 3 & 0 & 2\sqrt{2} & 0 \\ 0 & 0 & 0 & 2\sqrt{2} & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{pmatrix} \end{split}$$

and

$$\sum_{n,m} \langle n | \hat{J}_{y} | m \rangle \Rightarrow \frac{i}{2} \begin{pmatrix} 0 & -\sqrt{5} & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & -2\sqrt{2} & 0 & 0 & 0 \\ 0 & 2\sqrt{2} & 0 & -3 & 0 & 0 \\ 0 & 0 & 3 & 0 & -2\sqrt{2} & 0 \\ 0 & 0 & 0 & 2\sqrt{2} & 0 & -\sqrt{5} \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{pmatrix}$$
(3.11)

then the transition probabilities $|\langle n | \hat{J}_{\alpha} | m \rangle|^2$ may be calculated from the eigenvectors $|m\rangle$ of the diagonalized Hamiltonian via

$$|\langle n|\hat{J}_{\alpha}|m\rangle|^{2} = \left|\sum_{i,j} \langle n|j\rangle \langle j|\hat{J}_{\alpha}|i\rangle \langle i|m\rangle\right|^{2}$$
(3.12)

Hence $|\langle n|\hat{J}_{\perp}|m\rangle|^2$ may be determined from (3.10) and the temperature dependence of the total paramagnetic scattering cross section [barn Ce⁻¹] calculated from the probability of finding the CEF-split energy levels occupied. Explicitly, from (3.9),

$$\sigma_{para} = \frac{2}{3} 4\pi (0.07265) \left(\frac{6}{7}\right)^2 \sum_{\omega_{mn}} |f(\kappa)|^2 \frac{k_f(\omega_{mn})}{k_i} \frac{e^{-\frac{E_n}{k_B T}}}{Z} |\langle n|\hat{J}_{\perp}|m\rangle|^2$$
(3.13)

where the substitutions $g_J = 6/7$, $(1.91e^2/2mc^2)^2 = 0.07265$ barn and

$$\rho_n = \frac{e^{\frac{-B_n}{k_B T}}}{Z} \tag{3.14}$$

with the partition function

$$Z = \sum_{n} e^{\frac{-E_n}{k_B T}} \tag{3.15}$$

have been employed. The sum is performed over all possible ω_{mn} where $\omega_{mn} = E_m - E_n$.

The 'integral' measurement on D7 counts all neutrons scattered into each analyzer over a period of time and is thus the sum of all elastic and inelastic scattering events. In order to compare directly the theoretical σ_{para} with the experimental observations on D7, the sum in (3.13) must take into consideration the energy dependence of the transmission of the supermirror analyzers, the cerium form-factor, the sample absorption and the detector efficiency. Such corrections have been described in detail by Schärpf et al. (1992) and have all been incorporated into the calculation of σ_{para} by (3.13). The experimental B_l^m parameters obtained from the analysis of magnetic susceptibility measurements and inelastic neutron scattering experiments on CeSi_x samples are listed in Table 3.4. The calculation of the σ_{para} expected to be observed on D7 has been performed for each set of B_l^m coefficients using an incident neutron wavelength of 4.8Å. The results are shown in Fig. 3.28 and illustrate how sensitive the temperature dependence of σ_{para} is to changes in the B_l^m coefficients. The B_l^m obtained from analysis of the temperature dependence of the magnetic susceptibility of $CeSi_x$ single crystals (Sato et al. and Pierre et al.) consistently indicate that the excited energy levels are separated from the ground state by approximately 290K and 330K. However, the B_l^m coefficients obtained from analysis of inelastic neutron scattering experiments are consistent between themselves but do not compare well with those of the former χ measurements, instead predicting a splitting of the two excited doublets by energies of approximately 290K and 600K above the ground state doublet.

	Reference	Sample	B_2^0 (meV)	$B_4^0 \;({ m meV})$	$B_4^4 (\mathrm{meV})$
(x)	Sato et al. (1988)	CeSi _{1.86}	-0.2374	0.0729	0.376
		CeSi _{1.70}	-0.3295	0.0740	0.386
(x)	Pierre et al. (1990a)	CeSi _{1.86}	-0.39	0.08	0.39
		CeSi1.71	-0.6	0.04	0.22
(INS)	Galera et al. (1989)	CeSi ₂	-1.55	0.0905	0.47
(INS)	Kohgi <i>et al.</i> (1990a)				
	(16K)	CeSi _{1.90}	-1.92	0.13	0.36
	(16K)	CeSi _{1.80}	-2.19	0.078	0.29
	(20K)	CeSi _{1.70}	-2.04	0.061	0.21
	(180K)	CeSi _{1.70}	-1.28	0.111	0.23

Table 3.4: Experimental CEF parameters for CeSi_x from analysis of magnetic susceptibility measurements (χ) and inelastic neutron scattering (INS) experiments.

In the following comparison, the B_l^m coefficients obtained from macroscopic measurements of the sample magnetization and which show less variation when determined in different experiments, will be used.

In Fig. 3.29 the theoretical σ_{para} as expected to be measured on D7 is compared to the average $\bar{\sigma}_{para}$, as defined by

$$\bar{\sigma}_{para} = 4\pi \overline{\left(\frac{d\sigma_{para}}{d\Omega}\right)} \tag{3.16}$$

that has been observed experimentally for $\text{CeSi}_{1.80}$ (F), $\text{CeSi}_{1.80}$ (NF) and $\text{CeSi}_{1.85}$. The theoretical calculations have been performed using the B_l^m parameters of Sato et al. (1988) for $\text{CeSi}_{1.86}$ (Table 3.4). For the $\text{CeSi}_{1.80}$ calculation an incident neutron energy of 3.5meV has been used and for $\text{CeSi}_{1.85}$ $E_{inc} = 2.5 \text{meV}$, in accordance with the experimental measuring conditions used on D7.

From the upper figure of Fig. 3.29, the $\bar{\sigma}_{para}$ of CeSi_{1.85} at lowest temperatures measured is in good agreement with that expected taking into account the effect of the crystalline electric-field. However, the experimental $\bar{\sigma}_{para}$ exhibits a far stronger temperature dependence than that expected. In contrast, the non-ferromagnetic CeSi_{1.80} (NF) sample exhibits a temperature dependence of $\bar{\sigma}_{para}$ that is in good



Figure 3.28: Theoretical temperature dependence of σ_{para} , as expected to be observed on D7, for CeSi_x. All calculations have been performed for an incident neutron wavelength of 4.8Å. For the σ_{para} calculated using the B_i^m coefficients obtained from magnetic susceptibility measurements (B_i^m from χ data) the solid line is the calculation for the B_i^m of Sato et al. (1988) and the dashed line is for the B_i^m of Pierre et al. (1990a). For the σ_{para} calculated for CeSi_{1.70} using the B_i^m from INS data, the solid line is the calculation for the B_i^m obtained from the fit of the INS profile at 20K, and the dashed line corresponds to the fitted parameters of the INS profile at 180K.



Figure 3.29: Comparison of the theoretical σ_{para} (solid line) and experimental $\bar{\sigma}_{para}$ measured on D7 as a function of temperature. For both of the theoretical calculations the B_l^m coefficients of Sato *et al.* (1988) have been used with $\lambda_{inc} = 5.7$ Å for CeSi_{1.85} and $\lambda_{inc} = 4.8$ Å for CeSi_{1.80}. The experimental $\bar{\sigma}_{para}$ of CeSi_{1.80} are illustrated by $\bullet = \text{CeSi}_{1.80}$ (F) and $\circ = \text{CeSi}_{1.80}$ (NF). In both cases the estimated standard deviations in $\bar{\sigma}_{para}$ are smaller than the markers used.

agreement with that expected on the basis of the CEF, whilst the magnitude of $\bar{\sigma}_{para}$ remains consistently lower than that expected between 1.5K and 100K by an average factor of 2.8. For CeSi_{1.80} (F) the $\bar{\sigma}_{para}$ at 300K is in reasonable accordance with the expected paramagnetic cross section. However, at 13K there is a significant enhancement observed for $\bar{\sigma}_{para}$, over and above that expected.

Chapter 4

Literature review and comparison of CeSi_x data

In the attempt to further the understanding of the structural and magnetic phase transitions within the CeSi_x system, it is useful to carry out a review of the experimental results of other independent research groups, for both magnetization and diffraction experiments and also measurements of bulk physical quantities such as the electrical resistivity and the specific-heat capacity. A review and comparison between such work and the experimental results of Chapter 3 is performed below.

4.1 Evidence for the structural instability of $\operatorname{CeSi}_{x} (1.80 \le x \le 2.00)$

It has been only during the past three years that the coexistence of two structural phases within CeSi_x samples has been observed and reported. Kohgi *et al.* (1990b), Madar *et al.* (1990) and Murashita *et al.* (1991) have each independently observed such phenomena within powder samples of $\text{CeSi}_{1.90}$, $\text{CeSi}_{1.86}$ and $\text{CeSi}_{1.85}$. In their reports, none of the authors make any reference to the respective proportion of silicon vacancies within the two low temperature phases, both considered to have the ThSi_2 -type structure and tetragonal symmetry, but rather distinguish them by the length of their *c*-axis crystal lattice parameter. Kohgi *et al.* report that the phase with the

smaller c-axis appears below approximately 200K and the relative proportion of this phase increases with decreasing temperature such that at 20K it accounts for 64% of the sample. Similarly, Madar et al. observe that a second phase appears in their CeSi_{1.86} sample between 200K and 280K that is characterized by a smaller c-parameter than the single phase at room temperature. The authors observe that between 200K and 80K the relative proportion of the second phase within the sample increases with decreasing temperature, below which it remains approximately constant at 67%. Both sets of observations are in good agreement with those in § 3.3 for CeSi_{1.85}. The fact that neither Kohgi et al. nor Madar et al. observe the coexistence of two phases in their samples at room temperature is considered here to be due to the lower resolution of their diffraction profiles. Though Madar et al. also used the D2B spectrometer at the ILL with $\lambda_{inc} = 1.594$ Å, measurements were not performed for scattering angles greater than $2\theta = 100^{\circ}$. It may be observed from Fig. 3.8 that measurements at higher 2θ 's are required to observe the coexistence of two phases at room temperature. For comparison, the refined lattice parameters of Madar et al. (1990) for $CeSi_{1.86}$ are shown in Fig. 4.1a along with the results obtained for CeSi_{1.85} from this investigation. In Fig. 4.1b the lattice parameters of CeSi₂ (Dijkman, 1982) are compared to the those of the silicon 'rich' phase observed in CeSi_{1.85} (§ 3.3). From the striking similarities observed within these figures for both the magnitude and temperature dependence of the lattice parameters, it is clear that the silicon 'rich' phase of CeSi_{1.85} does behave like a CeSi_x phase with silicon concentration $x \approx 2$, in accordance with the silicon lattice site occupations obtained from the refinements of § 3.3. Also, it would appear reasonable to suggest that the two low temperature phases coexisting within the CeSi_{1.86} sample of Madar et al. have an unequal distribution of silicon vacancies, one of the phases having a stoichiometry close to CeSi₂.

It is interesting to observe that for all reports where two phases are observed to exist within CeSi_x samples at low temperatures, the ratio of these two phases is consistently ≈ 2 : 1. All authors report that the relative proportion of the two phases is temperature dependent but there is some ambiguity as to whether the phase with the larger or smaller *c*-parameter is dominant at low temperatures. These uncertainties in the interpretation have been encountered already in § 3.3 and § 3.4 of this investigation on $\operatorname{CeSi}_{1.85}$, where the neutron diffraction experiments clearly show



Figure 4.1: Comparison of the temperature dependence of the lattice parameters of a) CeSi_{1.86} (Madar *et al.*, 1990) and CeSi_{1.85} (this investigation), b) CeSi₂ (Dijkman, 1982) and the CeSi_{1.85} silicon 'rich' phase (this investigation). In figure a) the two tetragonal phases in CeSi_{1.86} are represented by \bullet and \blacktriangle . In figure b) \bigstar = CeSi₂. In both figures the silicon 'rich' phase of CeSi_{1.85} is represented by a solid line and the silicon 'poor ' phase by a dashed line and a dot-dash line for the *b* lattice parameter.

Reference	Sample	Low temperature η	
	stoichiometry		
This work (ILL expt.)	CeSi _{1.85}	0.69(3)	
This work (SRS expt.)	CeSi _{1.85}	pprox 0.33	
This work (SRS expt.)	CeSi _{1.80} (NF)	pprox 0.33	
Kohgi et al. (1990b)	CeSi _{1.90}	0.64	
Murashita et al. (1991)	CeSi _{1.85}	> 0.5	
	CeSi _{1.90}	≈ 0.33	
Madar <i>et al.</i> (1990)	CeSi _{1.86}	pprox 0.33	
Lambert-Andron et al. (1991)	PrSi _{2.00}	0.74	
Mori et al. (1984)	CeSi _{1.7} Ga _{0.3}	≈ 0.67	

Table 4.1: The low temperature estimates of η , the fraction of the phase with the smaller *c*-parameter coexisting within CeSi_z, CeSi_{2-x}Ga_x and PrSi₂.

that the phase with the smaller c-parameter (the orthorhombic silicon 'poor' phase) is dominant at 1.5K whereas the x-ray diffraction experiment has the phase with the larger c-parameter dominant at 10K. Defining η to represent the fraction of the phase with the smaller c-parameter coexisting within a sample at low temperatures, a summary of the experimentally observed η 's is given in Table 4.1.

Evidence for the structural instability of CeSi₂

A review of the experimental literature on CeSi_x also provides evidence to suggest that CeSi_2 is itself crystallographically unstable. In the course of preparation of polycrystalline $\operatorname{CeSi}_x (1.83 \le x \le 2.00)$ samples for resistivity measurements, Dhar *et al.* (1987) reported that a metallographic examination of their $\operatorname{CeSi}_{2.00}$ sample revealed a small amount of a second phase ($\approx 2\%$) that did not disappear after a prolonged heat treatment. In another case, an attempt by Sato *et al.* (1988) to grow a single crystal from a melt of stoichiometric composition of CeSi_2 yielded a crystal whose composition was considered to be $\operatorname{CeSi}_{1.86}$, by comparison of the linear coefficient of the specific-heat capacity of the single crystal with those of polycrystalline samples.

Temp. (K)	Phase	a (Å)	ь (Å)	c (Å)	% of phase
					in CeSi _{2.16}
1.5	CeSi _{2.12(1)}	4.1522(1)	-	14.0421(3)	65(1)
	CeSi _{1.83(5)}	4.1624(3)	4.1531(3)	13.8440(3)	28(1)
	Si	5.4193(1)	-	-	7(1)
100	CeSi _{2.16(2)}	4.1600(1)	-	14.0331(3)	66(1)
	CeSi _{1.83(5)}	4.1701(3)	4.1617(3)	13.8362(5)	27(1)
	Si	5.4211(1)	-	-	7(1)

Table 4.2: Refinement parameters for CeSi_{2.16} (Kirkwood, 1989).

Dijkman (1982) has investigated the structural, magnetic and thermal properties of several rare-earth disilicides and suggests that CeSi₂ is not readily formed from the starting stoichiometric composition. The author references a large spectrum of lattice parameters measured by independent research groups on CeSi₂ samples as evidence for such a conclusion. Also, Dijkman concludes that an anomaly in the low temperature magnetic susceptibility of a CeSi₂ sample is the result of cerium ions having anomalous environments, some with a lower coordination than others due to silicon vacancies or other lattice defects.

Probably the most conclusive evidence for the structural instability of CeSi₂ comes from a neutron powder diffraction experiment on a CeSi_{2.16} sample (Kirkwood, 1989). In this experiment a surplus of silicon was used in the sample preparation of CeSi₂, sufficient to ensure that there was a small silicon impurity phase in the final sample. Analysis of the diffraction profiles showed that the bulk of the sample did not consist of a single CeSi₂ phase but instead two CeSi_x phases, one with the tetragonal ThSi₂type structure and a silicon concentration that consistently refined higher than 2.00, and the second an orthorhombic GdSi₂-type phase containing silicon vacancies within the lattice. The refinement lattice parameters are shown in Table 4.2.

Observations on other rare-earth disilicides and related pseudo-binary 'disilicides'

CeSi₂ is not the only disilicide known to be crystallographically unstable. A similar coexistence of two phases with the same spacegroup but differing temperature variation of their lattice parameters has been known for several years for PrSi₂ (Dijkman (1982), Pierre *et al.* (1990b) and Lambert-Andron *et al.* (1991)) and the related pseudo-binary 'disilicide' CeSi_{2-x}Ga_x (Mori *et al.*, 1984). The following literature review of experimental work on these compounds and rare-earth digermanides reveals several interesting correlations in their crystallographic and magnetic properties.

$\underline{\operatorname{PrSi}_2}$

The coexistence of two low temperature phases in praseodymium 'disilicide' has been observed by neutron powder diffraction, Lambert *et al.* (1991). Their refinements gave the composition of the two phases to be $PrSi_{1.95\pm0.05}$ and they concluded that although to a first approximation the phases could be considered as tetragonal with the space group $I4_1/amd$, there was evidence for a small orthorhombic distortion in at least one phase. The two samples ordered magnetically below 12K, one ferromagnetically and the other with a modulated magnetic structure. In both phases the ordered moments were in the basal *a-b* plane. An interesting point suggested by the authors was that the modulated magnetic structure could be related to a modulated ordering of silicon vacancies within this phase.

The refined lattice parameters of Lambert *et al.* (1991) for PrSi₂ are shown in Fig. 4.2a. Their temperature dependence is very similar to that shown in Fig. 4.1a for CeSi_{1.85} and CeSi_{1.86}. For comparison, the temperature dependence of the refined lattice parameters of LaSi₂ (Dijkman, 1982) and CeSi_{1.80} (F) (§ 3.3) are shown in Fig. 4.2b. Both the latter two samples are believed to be single phase. The similarity between the structural phase transition and coexistence of two phases in CeSi_x and PrSi₂ indicates that such a structural phase transition is driven by a crystallographic instability rather than being related to any change in valence state of the Ce³⁺ ions in CeSi_x.

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Figure 4.2: The temperature dependence of the lattice parameters of a) $PrSi_2$ (Lambert *et al.*, 1991) b) LaSi₂ (Dijkman, 1982) and CeSi_{1.80} (F) (this investigation). In figure b) LaSi₂ is represented by \bullet and CeSi_{1.80} (F) by the solid line.

$CeGe_2$ and $CeSi_{2-x}Ge_x$

Due to the similarity of the electronic configurations of silicon and germanium, it is not that surprising that both cerium disilicides and cerium digermanides exhibit similar types of crystal physics. The important difference between these non-metal atoms is their size, silicon having an electronic configuration of $[Ne]3s^23p^2$ whereas for germanium it is $[Ar]3d^{10}4s^24p^2$.

At present there are no reports of a crystallographic instability in CeGe₂ similar to that of CeSi₂ samples. However, CeGe₂ forms in the orthorhombic GdSi₂-type structure (Lahiouel *et al.* (1986), Yashima *et al.* (1982a)) and the latter authors do report the presence of superlattice spots in their electron diffraction pattern. Magnetic susceptibility and specific-heat measurements within these references illustrate just one magnetic phase transition within CeGe₂ at $T_c \approx 7K$. Contrary to the Ce-Si system where the ThSi₂-type structure is observed only for silicon 'rich' CeSi_x samples, for CeGe_x ($x \approx 1.6$) the ThSi₂-type structure is observed and this alloy orders ferromagnetically at 6K (Lambert-Andron *et al.*, 1990). This measurement was performed on a single crystal and this allowed the observed superlattice reflections in their diffraction pattern to be shown to have tetragonal symmetry and to be related to an ordering of germanium vacancies within the ThSi₂-type structure. One more important difference between CeGe_x and CeSi_x is that for the former the ferromagnetically ordered moments lie along the *c*-axis whereas for the latter, the ordered moments are consistently observed only in the *a-b* plane.

The observations on the pseudo-binary system $\text{CeSi}_{2-x}\text{Ge}_x$ are equally interesting in terms of the structural and magnetic changes observed as a function of x. The results of Lahiouel *et al.* are summarized in Table 4.3. It is remarked how the the introduction of germanium into the CeSi₂ lattice appears only to cause an expansion of the *a*-axis for $0 < x \leq 1.0$.

$CeGa_2$ and $CeSi_{2-x}Ga_x$

Gallium has the electronic configuration $[Ar]3d^{10}4s^24p^1$ and thus an atomic radius close in magnitude to that of germanium (1.21 and 1.22Å respectively). However,

Alloy	Structure	a (Å)	b (Å)	c (Å)	T_{c} (K)
	type				
CeSi2	ThSi2	4.190(2)	-	13.88(2)	+
$\mathrm{CeSi}_{1.8}\mathrm{Ge}_{0.2}$	ThSi₂	4.194(2)	-	13.86(2)	-
CeSi _{1.6} Ge _{0.4}	ThSi₂	4.201(2)	-	13.85(2)	-
CeSi _{1.5} Ge _{0.5}	ThSi₂	4.210(3)	-	13.86(2)	-
CeSi _{1.4} Ge _{0.6}	ThSi_{2}	4.212(2)	-	13.85(2)	4.3
$\mathrm{CeSi}_{1.2}\mathrm{Ge}_{0.8}$	ThSi_{2}	4.229(3)	-	13.86(2)	8.1
CeSiGe	GdSi₂	4.245(3)	4.230(3)	13.87(2)	9.5
CeSi _{0.6} Ge _{1.4}	GdSi₂	4.284(3)	4.236(3)	13.93(2)	9.4
CeSi _{0.4} Ge _{1.6}	$GdSi_2$	4.305(3)	4.247(3)	13.99(2)	9.3
CeGe _{2.0}	$GdSi_2$	4.340(2)	4.248(2)	14.05(2)	6.8
Ce3Ge5	ThSi_{2}	4.255(8)	-	14.08(5)	7.2

Table 4.3: Physical properties of CeSi_{2-x} Ge_x alloys (Lahiouel *et al.*, 1986)

unlike the digermanide, CeGa₂ forms with the hexagonal AlB₂-type structure and orders ferromagnetically at $T_c = 8.4$ K having undergone multiple magnetic phase transitions at 11.3K, 10.3K and 9.9K (Takahashi *et al.*, 1988). The pseudo-binary compound CeSi_{2-x}Ga_x forms in the ThSi₂-type structure for small x, similar to the germanium pseudo-binary, but with the significant difference that the coexistence of two isostructural phases is observed within the interval $0.2 \le x \le 0.5$ (Mori *et al.*, 1984). For $x \ge 0.5$ the ThSi₂-type structure was considered to be retained but with a 3.6% increase in volume for CeSi_{1.5}Ga_{0.5} compared to CeSi_{1.9}Ga_{0.1}. The room temperature lattice parameters of the two alloys were a = 4.236Å, c = 14.09Å and a = 4.186Å, c = 13.92Å respectively. The authors observed no detectable change in the two-phase nature of their samples following annealing at 800°C for three days.

The first interesting observation on $\text{CeSi}_{2-x}\text{Ga}_x$ is that magnetic susceptibility measurements (Mori *et al.*) and electrical resistivity measurements (Moshchalkov *et al.*, 1987a) on these alloys indicate a non-magnetic \rightarrow magnetic transition between $0.2 \leq x \leq 0.5$. For the moment there remains considerable uncertainty into the exact critical gallium concentration $x_{c'}$, since the former authors suggest it is near to x = 0.5 only from an extrapolation of $\chi(T)$ below 15K, whereas the latter illustrate magnetic order in their CeSi_{1.9}Ga_{0.1} sample but have no detailed diffraction analysis of their samples to confirm which concentrations exhibit the coexistence of two phases; they infer this occurs by reference to Mori *et al.*. In subsequent papers it is observed that the magnetically ordered regime in CeSi_{2-x}Ga_x extends up to $x_{c''} \approx 1.0 \rightarrow$ 1.1 (Moshchalkov *et al.*, (1987b) and Brandt *et al.*, (1988)). For greater gallium concentrations the alloys are paramagnets and thus far, no experiments have been performed to determine the structural parameters of these alloys for x > 1.0, or to determine at which higher concentration a magnetic ground state reappears, bearing in mind that CeGa₂ is magnetic.

The second interesting observation is that the ratio of the two phases in $CeSi_{1.7}Ga_{0.3}$ is 2:1 for the small volume and large volume phases respectively, identical to that observed in this investigation (§ 3.3) and by the authors discussed earlier (Table 4.1).

A comparison of the pseudo-binary $\operatorname{CeSi}_{2-x}\operatorname{Ge}_x$ and $\operatorname{CeSi}_{2-x}\operatorname{Ga}_x$ systems makes clear the importance of the electronic configuration and bonding of the non-metal sublattice on the crystallographic and magnetic properties of these alloys and CeSi_x . If the structural properties of $RESi_x$ systems are only governed by the size of the rare-earth ion, x and the temperature of the system (as is often considered the case within the literature) then there could be no reason for the different single-phase and dual-phase nature of these pseudo-binaries bearing in mind that the germanium and gallium atoms are of equivalent size. This point will be discussed in more detail in § 6.1 where explanations are presented to account for the observations above and the manner in which the size and electronic configuration of the non-metal atom affects the crystallographic and magnetic properties of CeSi_x .

4.2 Magnetic susceptibility measurements

The magnetic susceptibility measurements performed on single crystals of CeSi_{1.71} and CeSi_{1.86} (Sato *et al.* (1988) and Pierre *et al.* (1990a)) show strong anisotropy and reflect the importance of crystalline electric-field effects in CeSi_x. The results of Pierre *et al.* are illustrated in Fig. 4.3 and are in good agreement with those of Sato *et al.*

except for the magnitude of the anisotropy observed at room temperature (a similar difference is observed in the anisotropy of the electrical resistivity measured by the two groups on their respective single crystals, see § 4.5). This leads to a slight difference in the crystalline electric-field parameters that they report from a theoretical fit of their susceptibility data taking into consideration a crystalline electric-field Hamiltonian of the form

$$\mathcal{H}_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 \tag{4.1}$$

Their experimental B_l^m parameters have been listed in Table 3.4.

Fig. 4.4 illustrates the effective magnetic moment μ_{eff} for CeSi_x calculated from a fit of the Curie-Weiss law to the high temperature inverse magnetic susceptibility. All the results of Lawrence *et al.* (1982), Yashima *et al.* (1982a) & (1986), Mori *et al.* (1984), Dijkman *et al.* (1982), Shaheen *et al.* (1987), Dhar *et al.* (1987), Sato *et al.* (1988) and Pierre *et al.* (1990a) have been included. The measurements on paramagnetic CeSi_x samples have been distinguished from those on samples that order magnetically at low temperatures. The results of this investigation have been included separately and it may be seen that the significantly large μ_{eff} found for the CeSi_{1.80} (NF) sample (§ 3.2) is not unphysical when compared to other measurements on CeSi_x alloys. An explanation for the consistently high effective paramagnetic moments in these samples remains to be found.

4.3 Measurements of the ordered magnetic moment in CeSi_x ($x \leq 1.80$)

Magnetization measurements

Table 4.4 summarizes the observations made from measurements of the temperature dependence of the magnetization of CeSi_x samples. Though Pierre *et al.* (1990a) see evidence for only one magnetic transition within their $\text{CeSi}_{1.71}$ single crystal, they do state that their measurements were performed with low resolution in the temperature range involved and they do not rule out the possibility of a second transition. The



Figure 4.3: The inverse magnetic susceptibility of $\text{CeSi}_{1.71}$ and $\text{CeSi}_{1.86}$ single crystals with the field along the a- (×) or c-axis (\circ), courtesy of Pierre *et al.* (1990a).



Figure 4.4: The effective paramagnetic moments of CeSi_x samples calculated from a Curie-Weiss fit to the high temperature inverse magnetic susceptibility. \bullet indicates samples that are magnetically ordered at low temperatures whereas \diamond represents the paramagnetic samples. The results of this investigation are shown separately via \bullet and \circ respectively.

Reference	Sample	$T_c \text{ or } T_n (\mathbf{K})$	Spontaneous magnetization	
			$(\mu_B/{ m Ce})$	
Hill et al. (1992)	(pc) CeSi _{1.60}	10.6	-	
	(pc) CeSi _{1.65}	10.6	-	
	(pc) CeSi _{1.70}	11.8 & 13.5	0.14 at 5K	
	(pc) CeSi _{1.75}	11.9 & 13.5	0.16 at 5K	
	(pc) CeSi _{1.80}	12.1	0.22 at 5K	
	(pc) CeSi _{1.85}	9.7	0.10 at 5K	
Sato et al. (1985)	(sc) CeSi _{1.70}	12.4 & 13.7	0.45 (<i>a-b</i> plane)	
			0.07 (<i>c</i> -axis)	
Pierre et al. (1990a)	(sc) CeSi _{1.71}	12.5	0.47 (<i>a-b</i> plane)	
			< 0.015 (c-axis)	
This work	(pc) CeSi _{1.80}	12.5	0.07 at 2K	

Table 4.4: Observations from M(T) measurements on $CeSi_x$ single crystal (sc) and polycrystalline (pc) samples.



Figure 4.5: Magnetization of a single crystal of $\text{CeSi}_{1.70}$ along the *a* and *c*-axis, courtesy of Sato *et al.* (1985).

magnetization measurements performed on single crystals (Pierre *et al.* and Sato *et al.*, 1985) both reveal an ordered moment of $\approx 0.45\mu_B/\text{Ce}$ aligned in the basal *a-b* plane and no significant spontaneous magnetic component (< $0.07\mu_B$) along the *c*-axis. Measurements performed by Hill *et al.* (1992) on polycrystalline CeSi_x samples ($1.70 \leq x \leq 1.85$) show a spontaneous ordered moment of $\approx 0.15\mu_B/\text{Ce}$ at 5K. This is slightly larger than the $0.07\mu_B/\text{Ce}$ observed for CeSi_{1.80} (F) at 2K (§ 3.2).

Measurements of the field dependence of the magnetization of CeSi_x illustrate a saturation magnetization of $\approx 0.3 \rightarrow 0.6 \mu_B/\text{Ce}$ where the magnetization consistently increases for decreasing x (Yashima *et al.* (1982b), (1986) and Shaheen & Schilling (1987)). Only the measurements of Sato *et al.* on their single crystal of $\text{CeSi}_{1.70}$ revealed a significant 'kink' in their M(H) curves for the magnetization along the *a*-axis, as illustrated in Fig. 4.5.

Neutron diffraction refinements

Sato *et al.* (1985) have performed a neutron diffraction experiment on a CeSi_{1.70} single crystal. At a temperature of 8K, their best fit to the observed magnetic scattering intensity is given by a ferromagnetically ordered moment of $0.5(1)\mu_B$ /Ce along the [021] or [201] directions of the ThSi₂-type crystal structure. In addition, they also observe that the ferromagnetic ordering, which develops below 13.7K, undergoes a weak antiferromagnetic modulation below 12.4K, the period of which is the same as that of the chemical unit cell along the *c*-axis. The magnitude of the antiferromagnetic component is estimated to be nearly 8% of the ferromagnetic component.

The magnitude of the ordered ferromagnetic moment observed for the CeSi_{1.70} single crystal is in very good agreement with that observed for CeSi_{1.80} (F) by neutron powder diffraction (§ 3.3). However, in both cases the ordered moment is smaller than the $\approx 1.07 \mu_B/\text{Ce}$ expected at 1.5K, taking into consideration the effect of the crystalline electric-field.



Figure 4.6: γ for CeSi_x as a function of x; • = Yashima *et al.* (1982c), \triangle = Dijkman *et al.* (1982) and \diamond = Gschneidner, Jr. *et al.* (1989). The solid line is a guide to the eye.

4.4 Measurements of the specific-heat capacity

As discussed in § 1.2, the specific-heat capacity at low temperatures is given by

$$c_v = \gamma T + \beta T^3$$

and thus the coefficient γ may be obtained experimentally from a graph of (c_v/T) versus T^2 by an extrapolation of a least-squares fit to the data. Fig. 4.6 illustrates the extrapolated γ 's for three independent measurements of the specific-heat capacity of CeSi_x as a function of silicon concentration. Comparing the results for CeSi_x with the neighbouring rare-earth disilicide LaSi₂ for which $\gamma \approx 6$ mJ/mol K² (Dijkman *et al.*, 1982), it is clear that there is a significant enhancement in the coefficient γ for all CeSi_x samples.

Within the uncertainty in the exact composition of the samples (all authors quote the starting stoichiometric composition of their samples and use room-temperature Xray diffraction (Yashima *et al.*, Dijkman) or metallographic examination (Gschneidner *et al.*) to determine that their sample is single phased), then all three data sets are in good agreement. Taking into consideration the possible errors in the exact stoichiometry of these samples, $\gamma(x)$ as a function of x may be reasonably assumed to follow the solid line shown in Fig. 4.6. The maximum in γ occurs for a silicon concentration of $x = 1.83(\pm 1)$. The experiment of Gschneidner *et al.* (1989) in

Reference	Sample	Temperature of anomaly
		in c_v (K)
Yashima & Satoh (1982)	(pc) CeSi _{1.80}	9.0
	(pc) CeSi _{1.70}	10.9
Yashima et al. (1986)	(pc) CeSi _{1.83}	6.2
	(pc) CeSi _{1.82}	6.7
	(pc) CeSi _{1.81}	6.7
Sato et al. (1988)	(sc) CeSi _{1.70}	12.4 & 13.7

Table 4.5: The low temperature anomalies observed in the specific-heat capacity of $CeSi_x$ alloys; (sc) denotes single crystal and (pc) polycrystalline samples.

which the specific-heat capacity is measured for a large number of CeSi_x samples in the concentration range $1.82 \leq x \leq 1.90$ indicate that there is probably no discontinuity in γ at the critical non-magnetic \rightarrow magnetic transition concentration ($x_c \approx 1.80$) but only a maximum. The former idea was put forward by Yashima *et al.* (1982c) after an extrapolation of their own measurements.

Recalling the definition of the coefficient γ in (1.7), an enhanced γ is usually interpreted as indicating a large density of states at the Fermi level due to the proximity of the narrow cerium 4f band to the Fermi level. The enhancement of γ as a function of x has been attributed to fast spin-fluctuations in the CeSi_x system as x approaches the critical concentration x_c of the magnetic instability (Yashima *et al.* (1982c) & Dhar *et al.* (1987)). They argue that as the silicon concentration is further reduced, the RKKY interaction is sufficient to stabilize the moment and the CeSi_x alloys have a magnetically ordered ground state. Here, however, an alternative explanation is developed in which the 4f electrons play an insignificant role in the further enhancement of $\gamma(x)$ as $x \to x_c$. This discussion is presented in full in § 6.1.

Table 4.5 lists the temperatures at which anomalies are observed in the low temperature specific-heat of CeSi_x samples.

4.5 Electrical resistivity measurements

The preparation of small rectangular samples of CeSi_x to be used for resistivity measurements is a difficult task due to the brittleness of these alloys. There is a consistent tendency for cracks to form in polycrystals that hinder the extraction of good 'needle' shaped samples. This fact led some authors to conclude that anomalies observed in the electrical resistivity, $\rho(T)$, of polycrystalline samples in the non-magnetic temperature regime are due to crack formation. However, measurements on single crystals indicate that such anomalies are inherent properties of CeSi_x alloys and should not be overlooked. An overview of the resistivity measurements that have been performed on both single crystal and polycrystalline CeSi_x samples is given below.

Fig. 4.7 illustrates the resistivity measurements of Pierre *et al.* (1990a) on two single crystals of CeSi_x. These results provide a good illustration of the types of temperature dependence observed for $\rho(T)$ in the CeSi_x system. The measurements of Pierre *et al.* are in fair agreement with those of Sato *et al.* (1988) who have also performed measurements on single crystals samples of CeSi_x x = 1.70, 1.86 (though it must be stated that the latter authors have only ascribed the composition of their single crystals by a tentative comparison of the linear specific-heat coefficient γ of these samples to the approximate $\gamma(x)$ dependence suggested by Yashima *et al.*, 1982c). The significant differences between the two data sets are the magnitude of the anisotropy observed in the resistivity at room temperature, with Sato *et al.* observing no anisotropy in either of their single crystals, and the temperature at which there is a crossing of ρ_a and ρ_c in CeSi_{1.86}, the latter authors observing this cross-over at $T \approx 175$ K.

To a first approximation, it is possible to consistently categorize all of the experimental results on CeSi_x alloys into three groups. Each group (type '1', '2' and '3') has a distinctly different temperature variation of $\rho(T)$ as shown schematically in Fig. 4.8. Table 4.6 lists the most recent resistivity measurements performed on CeSi_x alloys by independent research groups. It summarizes the temperatures of the discontinuities observed in the gradient of $\rho(T)$, for the warming cycle in the cases where both cycles were measured, for T > 200K (it must be stressed that this data has been extracted by hand from the published results and that the original references


Figure 4.7: Resistivities of $\text{CeSi}_{1.71}$ and $\text{CeSi}_{1.86}$ single crystals for the current along the *a*-axis $(I \parallel a)$ or *c*-axis $(I \parallel c)$, courtesy of Pierre *et al.* (1990a).



Figure 4.8: Schematic representation of the three types of temperature dependence of $\rho(T)$ observed for CeSi_x alloys.

should be consulted before inferring that the authors themselves have cited all such anomalies in ρ). The magnetic ordering temperature of the samples is listed along with the type of temperature dependence observed for $\rho(T)$.

The 'grouping' of the experimental data in the manner described above is only approximate but it does allow some interesting correlations to be observed.

- Apart from the small anomaly observed in the single crystal of $\text{CeSi}_{1.71}$ (\approx 230K) there are no obvious high temperature anomalies observed in $\rho(T)$ for samples that are magnetically ordered at low temperatures and have the type '1' temperature dependence.
- For samples that are stoichiometrically close in concentration to the critical concentration ($x_c \approx 1.80$) and for which some are found to be magnetically ordered and others not, the temperature dependence of $\rho(T)$ consistently follows that classed as type '2'.
- Samples with a stoichiometric concentration x ≥ 1.88 consistently have a type
 '3' temperature dependence of ρ(T) (bearing in mind that the weight loss during the sample preparation of Hill et al. (1992) could justifiably result in the sample quoted as CeSi_{1.90} having a true stoichiometry as low as CeSi_{1.83}).

Before continuing to discuss the possible implications of these observations, the results of Gschneidner, Jr. *et al.* (1989) should also be mentioned. In their paper they report resistivity measurements on the CeSi_{1.84}, CeSi_{1.85} and CeSi_{1.86} alloys of Lee *et al.* (1987) and also on several other alloys in the concentration range $1.84 \le x \le 1.86$. Their results fit in well with the classification scheme above with a type '2' temperature dependence observed for all of their samples. However it is considered here that their comparison between polycrystalline samples with an initial stoichiometry of CeSi_{1.852}, CeSi_{1.855}, CeSi_{1.856} etc. ... is over optimistic bearing in mind that the authors admit to weight losses of up to 0.3% during sample preparation. Assuming a 0.2% silicon weight loss from a sample of initial stoichiometry CeSi_{1.856} would give a final sample of CeSi_{1.842}. This point will be returned to further on in this discussion. For now, it is simply remarked that the results of Gschneidner *et al.* (1989) do correlate with those in Table 4.6.

Reference	Sample	<i>T</i> _c (K)	$T_{\rm anomaly} \pm 3 ({\rm K})$	Type
Sato et al. (1988)	(sc) CeSi _{1.86}	-	$\rho_a:255 \ \rho_c:243$	3
	(sc) CeSi _{1.70}	12.1, 13.5	-	1
Pierre et al. (1990a)	(sc) CeSi _{1.86}	-	ρ_a :235, 261 ρ_c :250	3
	(sc) CeSi _{1.71}	12.0, 13.3	$ ho_a$:225	1
Lee et al. (1987)	(pc) CeSi _{1.90}	-	230, 264	3
	(pc) CeSi _{1.88}	-	261	3
	(pc) CeSi _{1.86}	-	213, 236	2
	(pc) CeSi _{1.85}	1.0	224, 242	2
	(pc) CeSi _{1.84}	5.1	211	2
	(pc) CeSi _{1.83}	5.5	-	1
	(pc) CeSi _{1.82}	8.4	-	1
	(pc) CeSi _{1.80}	12.6	-	1
	(pc) CeSi _{1,75}	11.9	-	1
	(pc) CeSi _{1.72}	11.6	-	1
	(pc) CeSi _{1.70}	11.6	-	1
	(pc) CeSi _{1.67}	11.8	-	1
Sakurai et al. (1990)	(pc) CeSi _{2.00}	-	290	3
Hill et al. (1992)	(pc) CeSi _{2.00}		210	3
	(pc) CeSi _{1.95}	-	240	3
	(pc) CeSi _{1.90}	-	226, 290	2
	(pc) CeSi _{1.85}	9.7	-	1
	(pc) CeSi _{1.80}	12.1	-	1
	(pc) CeSi _{1.75}	11.9	-	1
	(pc) CeSi _{1.70}	11.8	-	1

Table 4.6: Summary of resistivity measurements on single crystal (sc) and polycrystalline (pc) samples of CeSi_z.

All type '3' samples are non-magnetic and to a reasonable approximation their $\rho(T)$ curves follow the normal temperature dependence expected for such samples, as discussed in § 1.2. The only significant difference are the presence of the anomalies observed in $\rho(T)$ between 200 and 300K. Gschneidner *et al.* (1989), and subsequently Hill *et al.* (1992) do not attribute these features to crystallographic distortions within their samples since the powder X-ray diffraction experiments performed by Gschneidner *et al.* (id not reveal the presence of a second phase within their samples. Conversely, Pierre *et al.* (1990a) have subsequently published the results of the coexistence of two structural phases in CeSi_{1.86} powder samples (Madar *et al.*, 1990) and in their case they do link the presence of the $\rho(T)$ anomalies to structural transformations within their sample. Overall, in light of the results of § 3.3 and § 4.1, it would appear very justifiable to link the existence of the high temperature anomalies in $\rho(T)$ to structural phase transitions in these samples. Indeed such resistivity measurements provide further proof for the crystallographic instability of CeSi_x (1.80 $\leq x \leq 2.00$) phases.

For the type '1' samples, all of which exhibit magnetic ordering, the steep drop in the low temperature resistivity correlates very well with the magnetic ordering temperatures in these samples, and thus is well understood. However the consistent tendency for $\rho(T)$ to decrease with increasing temperature remains to be given a consistent explanation.

The type '2' behaviour of $\rho(T)$ does have a resemblance to a superposition of types '1' and '3', consistent with some of the samples exhibiting magnetic order. However before attempting to understand such a temperature dependence, the large variation in the magnitude of ρ should be taken into consideration. Hill *et al.* (1992) noted that the room temperature resistivity of their CeSi_{1.90} sample was more than a factor of 100 greater than any of the other CeSi_x samples in their series, the latter varying from each other by no more than a factor of three. The authors subsequently repeated their measurements on other CeSi_{1.90} samples cut from the same ingot and found that while they illustrated approximately the same form of temperature dependence, the $\rho(300)$ values were now nearly in line with the other members of their series, one being a factor of ten larger and the second of the same order of magnitude. A similar sample dependence of the resistivity was observed by Gschneidner *et al.* (1989) when they performed resistivity measurements on nine CeSi_x alloys in the concentration range $1.84 \leq x \leq 1.86$ and found a significant increase in the magnitude of ρ for some samples in comparison to others. As mentioned previously, it is not considered here that it is feasible to do a comparison of their results as a function of x due to the large uncertainty in the exact composition of their samples in relation to their very small differences in starting stoichiometry. However, taking all such samples into consideration, the magnitude of the resistivity of all type '2' samples (between $900 \rightarrow 5000\mu\Omega$ cm) is significantly larger than all the type '1' and '3' samples in Table 4.6 whose room temperature resistivity ranges from $100 \rightarrow 1000\mu\Omega$ cm but never surpasses this upper bound.

Overall, the tendency for an enhancement of the resistivity of samples with a type '2' temperature dependence would appear to be a real phenomenon, having been observed in several independent samples. It has also been observed in the pseudo-binary $\operatorname{CeSi}_{2-x}\operatorname{Ga}_x$ system at a concentration of $x \approx 1.0$, approximately the critical concentration $x_{c'} \approx 1.0 \rightarrow 1.1$ separating alloys that have magnetically ordered ground states from those that are paramagnetic (Brandt *et al.*, 1988). In the latter case, measurements were made of the Hall coefficient and this too was found to undergo a similar enhancement at the same concentration.

4.6 Summary

The preceeding review highlights several conflicting results existing in the literature regarding the exact critical silicon concentration x_c separating CeSi_x samples with magnetic or non-magnetic ground states, and also the crystallographic structure of CeSi_x samples in the concentration range $1.80 \leq x \leq 1.85$. Such differences partly arise from the uncertainty in the exact composition of the CeSi_x samples used, e.g. Hill *et al.* (1992) state that due to silicon loss during sample preparation the true silicon content of their samples may be up to several percent lower than the initial stoichiometric concentration that they have taken to 'label' their samples with, thus their 'CeSi_{1.90}' sample may realistically have a true stoichiometry of CeSi_{1.83}. Differences also arise as a result of the experimental resolution and temperature by

which the lattice parameters of the alloys are determined. In view of the subtle nature of the phase separation and distortion observed within CeSi_x samples in Chapter 3, it is to be expected that only high resolution X-ray or neutron diffraction analysis, both at and below room temperature, will be sufficient to characterize CeSi_x alloys. This point should be borne in mind when reading and making comparisons between published work on CeSi_x .

The observation of the coexistence of two structural phases within independent $\operatorname{CeSi}_x (x = 1.85, 1.86 \text{ and } 1.90)$ samples and the large number of high temperature anomalies in the electrical resistivity of $\operatorname{CeSi}_x (1.80 \leq x \leq 2.00)$ samples both support the crystallographic instability of such samples and the experimental observations described in § 3.3 and § 3.4. In view of the evidence suggesting that CeSi_2 is itself crystallographically unstable, it appears unlikely that the crystallographic instability of CeSi_x is the result of introducing silicon vacancies into the crystal structure. The observation of similar structural phase transitions occurring in PrSi_2 and $\operatorname{CeSi}_{2-x}\operatorname{Ga}_x (0.2 < x < 0.5)$ suggest that the crystallographic instability of $\operatorname{CeSi}_x (1.80 \leq x \leq 2.00)$ is not related to a change in the valence state of the cerium ions but is greatly influenced by the electronic configuration and the bonding of the non-metal atoms (Si, Ga) within the silicon sublattice.

Both the diffraction and the electrical resistivity experiments support the stability of CeSi_x ($x \leq 1.80$) samples with the orthorhombic GdSi₂-type structure. Neither indicate the existence of structural phase transitions in these alloys, almost all of which are magnetically ordered at low temperatures. Indeed the preceeding review consistently illustrates the close correspondence between the critical silicon concentration at which the cross-over from the tetragonal ThSi₂-type \rightarrow orthorhombic GdSi₂-type structure occurs ($1.80 \leq x_{cs} \leq 1.85$) and the critical concentration separating CeSi_x samples with magnetic or non-magnetic ground states ($x_c \approx 1.80$).

The review of the magnetization and specific-heat measurements on CeSi_x ($x \leq 1.80$) alloys indicate the existence of two magnetic phase transitions within many of these samples. For the $\text{CeSi}_{1.70}$ single crystal of Sato *et al.* (1985) these have been identified as ferromagnetic order ($T_c = 13.7$ K) onto which is superposed a weak antiferromagnetic modulation ($T_N = 12.4$ K).

Chapter 5

Discussion of the structural and magnetic phase transitions in $CeSi_x$ within Landau theory

In this chapter the Landau theory of phase transitions is applied to the temperature dependent structural and magnetic phase transitions observed within CeSi_x . The aim of the discussions is to determine which types of phase transition are possible in CeSi_x , subject to the symmetry constraints, and thus to provide a greater understanding of the physical processes involved in such transitions. In applying the Landau theory, the text of Tolédano & Tolédano (1987) has been followed and the reader is referred to this text for a more thorough description of the concepts and techniques used below. The following two sections consider the structural and magnetic phase transitions in turn.

5.1 Structural phase transitions in $CeSi_x$

The neutron and X-ray synchrotron powder diffraction experiments described in § 3.3, § 3.4 and § 4.1 have shown that $\operatorname{CeSi}_x(1.80 \leq x \leq 2.00)$ samples are crystallographically unstable. For samples in the compositional range $1.80 \leq x \leq \approx 1.90$, at high temperatures these are single phase with the ThSi₂-type crystal structure

 $(GdSi_2) = GdSi_2$ -type structure 600 $1.80 \leq x_{cs} \leq 1.85$ $x'_{c} = ?$ Single phase. femperature, T [K] 400 (ThSi₂) Evidence of difficulty in preparation of Single phase. single phase Coexistence (GdSi2) 200 of 2 phases with samples. unequal silicon (ThSi,) concentrations. (ThSi₂) + (GdSi2) 0 1.60 1.70 1.80 1.90 2.00 Silicon concentration, x

 $(ThSi_2) = ThSi_2$ -type structure

Figure 5.1: Schematic illustration of the proposed structural phase diagram for CeSi_x (1.60 $\leq x \leq 2.00$).

(space group $I4_1/amd$) and a random distribution of silicon vacancies on the silicon lattice sites. As the sample temperature is decreased then at a certain critical temperature (T_{cs}) a phase separation occurs into two phases with an unequal proportion of silicon vacancies. One of the phases has a stoichiometry close to CeSi₂ and retains the ThSi₂-type structure of the high temperature single phase. The second phase has a larger proportion of silicon vacancies than in the high temperature phase and the GdSi₂-type structure (space group Imma). At the present time, there is experimental evidence to suggest that CeSi₂ is crystallographically unstable but a temperature dependent phase separation similar to the one described above has not yet been observed. Meanwhile, all experiments show that CeSi_x ($x \leq 1.80$) samples with the GdSi₂-type structure are stable, single phase samples at all temperatures. In view of these observations it is proposed that the structural phase diagram of CeSi_x (1.60 $\leq x \leq 2.00$), both as a function of temperature and silicon concentration, may be represented schematically by Fig. 5.1.

In the following discussion, only the temperature dependent structural phase transition in CeSi_x (1.80 $\leq x \leq \approx$ 1.90) samples will be considered. Algebraically, this reversible structural phase transition occuring at temperature T_{cs} may be represented (in accordance with (3.1)) by

$$(T > T_{cs}) \qquad (T < T_{cs})$$

CeSi_x $\Rightarrow \qquad \eta \text{CeSi}_y + (1 - \eta)\text{CeSi}_z \qquad (5.1)$

where CeSi_{y} represents the phase with the larger concentration of silicon vacancies, hereby referred to as the silicon 'poor' phase, CeSi_{z} represents the phase with the smaller concentration of silicon vacancies, referred to as the silicon 'rich' phase, and η represents the relative proportion of the two phases coexisting in the sample at low temperatures. The experimental observations have shown that the fraction η is temperature dependent, i.e. $\eta = \eta(T)$. Furthermore, while the silicon 'rich' phase has the tetragonal ThSi₂-type structure in which all the silicon lattice sites are equivalent, the silicon 'poor' phase has the orthorhombic GdSi₂-type structure and a preferential ordering of silicon vacancies on one of the two inequivalent silicon lattice sites.

In view of the experimental observations summarized above, there are two processes involved within the temperature dependent structural phase transition of CeSi_x $(1.80 \leq x \leq \approx 1.90)$ samples that require to be understood. Firstly, a low temperature phase separation into two tetragonal phases with an unequal proportion of silicon vacancies. Secondly, an orthorhombic distortion and subsequent ordering of vacancies within one of these phases, the silicon 'poor' phase. The discussion below considers each of these processes in turn.

Low temperature phase separation in $\operatorname{CeSi}_{x}(1.80 \leq x \leq \approx 1.90)$ samples

An insight into the low temperature phase separation of $\operatorname{CeSi}_x(1.80 \leq x \leq \approx 1.90)$ samples may be obtained by considering the thermodynamic properties of the CeSi_x system. For any system at constant temperature and pressure it is the stable minimum of the Gibbs free energy (\mathcal{G}) that determines the equilibrium state of the system. At a temperature T the Gibbs free energy is defined by

$$\mathcal{G} = H - TS \tag{5.2}$$

where S is the entropy and H the enthalpy of the system. The entropy will have a thermal contribution and a configurational contribution, as discussed in more detail below. The enthalpy is a measure of the heat content of the system and is given by

$$H = U + PV \tag{5.3}$$

where U is the internal energy, P is the pressure and V is the volume of the system. The internal energy U arises from the vibrational energy of the atoms in the system and the interaction energy (bonding) between the atoms. When a transformation occurs within a solid in which heat is absorbed or evolved, the change in the PVterm in (5.3) at constant pressure is generally very small in comparison to U. Thus the approximation $H \approx U$ and

$$\mathcal{G} = U - TS \tag{5.4}$$

may be employed. The equilibrium state of the system will be determined by that state for which the Gibbs free energy is a minimum. From (5.4), it is evident that at high temperatures the TS term will be significant in determining the free energy of the system. For the minimum free energy at high temperatures, the entropy of the system should be maximized. Conversely, at low temperatures it will be the contribution of the internal energy that has the significant effect on the Gibbs free energy of the system. This will be demonstrated qualitatively, below.

A phase separation is considered from a single high temperature CeSi_x

 $(1.80 \le x \le \approx 1.90)$ phase with the ThSi₂-type structure into two low temperature phases that have different concentrations of silicon atoms but which both retain the same crystal structure as the high temperature phase. To a first approximation, if we neglect the cerium sublattice, considering it to remain invariant during the phase separation, and consider only the changes in the silicon crystal sublattice, the two low temperature phases differ only by their relative concentrations of silicon atoms and silicon vacancies. This situation may be mapped onto the model of a regular binary solid solution (Porter & Easterling, 1992). Rather than consider the mixing of two types of atom A and B that have the same crystal structures in their pure states as in a solid solution, here we consider a mixture of silicon atoms (A) and silicon vacancies (B). The regular solution model considers that 1 mol of homogeneous solid solution is made by mixing X_A mol of A and X_B mol of B. Thus

$$X_A + X_B = 1 \tag{5.5}$$

and X_A and X_B are the mole fractions of A and B respectively in the alloy. The mixing is considered to be performed in two steps:-

- 1. X_A mol of pure A and X_B mol of pure B are brought together.
- 2. The atoms A and B are allowed to mix together to form a homogeneous solid solution.

The Gibbs free energy of the system after step 1 is given by

$$\mathcal{G}_1 = X_A \mathcal{G}_A + X_B \mathcal{G}_B \tag{5.6}$$

where \mathcal{G}_A and \mathcal{G}_B are the molar free energies of pure A and pure B at the temperature and pressure of the above experiment. The free energy of the system will change during the mixing of the atoms in step 2 and the Gibbs free energy of the solid solution can be expressed as

$$\mathcal{G}_2 = \mathcal{G}_1 + \Delta \mathcal{G}_{mix} \tag{5.7}$$

where $\Delta \mathcal{G}_{mix}$ is the change in the Gibbs free energy caused by the mixing. Since

$$\mathcal{G}_1 = U_1 - TS_1$$
$$\mathcal{G}_2 = U_2 - TS_2$$

then putting

$$\Delta U_{mix} = U_2 - U_1$$
$$\Delta S_{mix} = S_2 - S_1$$

from (5.7) we have

$$\Delta \mathcal{G}_{mix} = \Delta U_{mix} - T \Delta S_{mix} \tag{5.8}$$

 ΔU_{mix} is the energy absorbed or evolved during step 2 and ΔS_{mix} is the difference in entropy between the mixed and unmixed states. For mixing to occur it is necessary that

$$\Delta \mathcal{G}_{mix} = \mathcal{G}_2 - \mathcal{G}_1 < 0 \tag{5.9}$$

Considering the ΔS_{mix} term in (5.8), in statistical thermodynamics the entropy of a system is given by

$$S = k_B \ln w \tag{5.10}$$

where k_B is the Boltzmann constant and w is a measure of the randomness of the system. There are two contributions to the entropy of a solid solution, a thermal contribution S_{th} and a configurational contribution S_{config} . For S_{th} , w is the number of ways in which the thermal energy of the solid solution can be divided among the atoms. For S_{config} , w is the number of distinguishable ways of arranging the atoms in the solid solution. If there is only a small volume change or heat change during the mixing, the significant contribution to ΔS_{mix} is the change in configurational entropy. Thus

$$\Delta S_{mix} = k_B \ln \left(\frac{(N_A + N_B)!}{N_A! N_B!} \right) \tag{5.11}$$

Introducing Stirling's approximation $(\ln N! \approx N \ln N - N)$ into (5.11) and substituting for $N_A = X_A N_a$ and $N_B = X_B N_a$ where N_a is Avogadro's number, it follows that

$$\Delta S_{mix} = -k_B N_a \left(X_A \ln X_A + X_B \ln X_B \right) \tag{5.12}$$

As for the ΔU_{mix} term in (5.8), it is assumed that the only contribution to the heat of mixing is from bond energies between adjacent atoms in the solid solution. Furthermore, it is assumed that the interatomic distances and bond energies are independent of composition; all A-A bonds are taken to have an energy ϵ_{AA} , all B-B bonds have an energy ϵ_{BB} and A-B bonds have an energy ϵ_{AB} . It is considered that when the atoms are separated to infinity the system has zero energy. The ϵ_{AA} , ϵ_{BB} and ϵ_{AB} are negative quantities and become increasingly more negative as the bonds become stronger. Denoting P_{AB} to be the number of A-B bonds present in the solid solution, it may be shown (Gaskell, 1973) that

$$\Delta U_{mix} = P_{AB}\epsilon \tag{5.13}$$

where

$$\epsilon = \epsilon_{AB} - \frac{1}{2} \left(\epsilon_{AA} + \epsilon_{BB} \right) \tag{5.14}$$

It may also be shown that if ϵ is small then

$$\Delta U_{mix} = z N_a X_A X_B \epsilon \tag{5.15}$$

where z is the number of bonds per atom.

Substituting for ΔS_{mix} and ΔU_{mix} in (5.8), the free energy change on mixing of a regular solid solution is thus

$$\Delta \mathcal{G}_{mix} = z N_a X_A X_B \epsilon + T k_B N_a \left(X_A \ln X_A + X_B \ln X_B \right)$$
(5.16)

Equation (5.16) may be used to demonstrate qualitatively the relative importance of the internal energy and entropy contributions in determining the minimum of the Gibbs free energy of the system. Fig. 5.2 gives a schematic illustration of $-T\Delta S_{mix}$, ΔU_{mix} and $\Delta \mathcal{G}_{mix}$ as calculated from (5.12), (5.15) and (5.16) respectively for the two cases $\epsilon > 0$ and $\epsilon < 0$, and for both low and high T. The figures clearly show the increased importance of the entropy term in determining the Gibbs free energy of the system at high T.

In the case of CeSi_x , A represents a silicon atom and B represents a silicon vacancy in the silicon crystal sublattice. Thus ϵ_{AA} is the bond energy between two silicon atoms, ϵ_{BB} is zero, ϵ_{AB} is the energy associated with a silicon 'dangling-bond' (i.e. the energy associated with an extra un-paired electron on a silicon atom that previously had three of its four $3s^23p^2$ electrons involved in covalent bonds with neighbouring silicon atoms) and from (5.14),

$$\epsilon = \epsilon_{AB} - \frac{1}{2} \epsilon_{AA} \tag{5.17}$$

For the situation where $\epsilon < 0$, Figures 5.2a and 5.2b illustrate that, both at high and low temperatures, the minimum of the Gibbs free energy corresponds to an equal 50:50 mixing of the silicon atoms and silicon vacancies throughout the solid solution in a random, homogeneous manner. For the situation where $\epsilon > 0$, Fig. 5.2c illustrates that at high temperatures the same result applies. The dominant factor in the minimization of the free energy of the system is the maximization of the mixing entropy, brought about by the random mixing of all silicon atoms and silicon vacancies over all of the possible sites in the silicon sublattice. However, at sufficiently low temperatures, a situation will be reached such as that shown in Fig. 5.2d. In this case, the minimum of the free energy of CeSi_x occurs for an uneven proportion of silicon atoms and vacancies throughout the sublattice. As such, the free energy of the solid solution could be minimized by a separation into two phases, in each of which the maximum ordering of silicon atoms or vacancies could occur.



Figure 5.2: Qualitative illustration of the energy changes on mixing $-T\Delta S_{mix}$, ΔU_{mix} and $\Delta \mathcal{G}_{mix}$ calculated by the regular solid solution model (courtesy of Porter & Easterling, 1992). The calculations are performed for; a) $\epsilon < 0$ and high T, b) $\epsilon < 0$ and low T, c) $\epsilon > 0$ and high T, and d) $\epsilon > 0$ and low T.

The discussion above is simple and qualitative but it illustrates the situation in which a low temperature phase separation of CeSi_x would be expected. If a danglingbond on a silicon atom is energetically less favourable than the covalent bond between two neighbouring silicon atoms, then $\epsilon > 0$ and at sufficiently low temperatures $(T < T_{cs})$ a phase separation should occur. One of the phases will have a greater proportion of silicon vacanices, thereby minimizing the number of dangling-bonds in the second phase. Furthermore, if there is an orthorhombic distortion within the phase with the larger concentration of silicon vacancies such that there are two inequivalent types of silicon lattice sites, one higher in energy than the other, a preferential ordering of the silicon vacancies on the higher energy lattice sites would further minimize the free energy of the system. At this stage, little more may be said concerning the low temperature phase separation within CeSi_x (1.80 $\leq x \leq \approx 1.90$) samples without performing quantitative calculations, such as band-structure calculations, the scope of which is beyond the limits of this thesis. To pursue the second part of this discussion, i.e. a qualitative discussion of the orthorhombic distortion and ordering of silicon vacancies observed within the silicon 'poor' phase at low temperatures, the phenomenological theory of Landau will be used. The discussion below first introduces the Landau theory and then uses it to discuss the possible types of structural phase transition that, following the low temperature phase separation, may subsequently occur within the silicon 'poor' phase.

Introduction to Landau theory

Landau was first to draw attention to the fact that at any second-order phase transition a symmetry change occurs within the system. The method he proposed for analyzing the behaviour of a system in the vicinity of a second-order phase transition is known as *Landau theory* and is described in detail by Landau & Lifshitz (1980). A short review of the essential features of Landau theory is given below.

The Landau theory introduces the concept of an order-parameter, η_{ii} , that specifies a new physical property of a system that arises following a phase transition from an initial phase where this property was absent. Thus η_{ii} is defined such that it is zero on one side of the phase transition and finite on the other. As the theory was derived for continuous second-order phase transitions, the continuity of the change of state in such a phase transition gives that η_{ii} takes arbitarily small values near the transition point. Correspondingly, in the neighbourhood of this point, the free energy of a system $\mathcal{G}(T, P, \eta_{ii})$ may be expanded in a Taylor series such that

$$\mathcal{G}(T, P, \eta_{ii}) = \mathcal{G}_0 + A_i \eta_{ii}^2 + B_i \eta_{ii}^4 + \dots$$
(5.18)

where \mathcal{G}_0 is the value of the potential in the initial phase and the coefficients A_i , B_i , ..., are functions of T and P. The expansion of the thermodynamic potential must be invariant with respect to the group of symmetry operations \mathcal{G}_0 characterizing the initial phase. For an arbitrary T and P, the value of η_{ii} is determined from the condition of thermal equilibrium, i.e.

$$\frac{\partial \mathcal{G}}{\partial \eta_{\iota i}} = 0 \tag{5.19}$$

$$\frac{\partial^2 \mathcal{G}}{\partial \eta_{ii}^2} > 0 \tag{5.20}$$

From (5.19) it is clear why there is no linear term in the expansion (5.18). The absence of a third-order term in η_{ii} reflects the fact that the theory has been developed for continuous second-order phase transitions; the presence of a cubic term in the thermodynamic potential inevitably leads to a first-order phase transition. The condition for the absence of third-order invariants in (5.18) is known as the *Landau condition* and it restricts that no order-parameters η_{ii} may be considered that transform according to the irreducible representation Γ_i of G_0 such that

$$(\Gamma_{\iota})^{3} \in \Gamma_{1} \tag{5.21}$$

From (5.20) the condition that the transition point itself is a stable state gives that the fourth-order term in (5.18) must be positive. Hence, at the critical temperature (T_{cs}) and pressure (P_{cs}) at which the phase transition occurs,

$$A_{\iota}(T_{cs}, P_{cs}) = 0, \quad B(T_{cs}, P_{cs}) > 0$$
(5.22)

In practice there are many sets of scalar quantities η_{ii} (i = 1,...) carrying the symmetry of the irreducible representation Γ_i of G_0 that may be considered in the expansion of the free energy, i.e.

$$\mathcal{G}(T, P, \eta_{\iota i}) = \mathcal{G}_0 + \sum_{\iota} A_{\iota} \left[\sum_{i} \eta_{\iota i}^2 \right] + \sum_{\iota} B_{\iota} \left[\sum_{i} \eta_{\iota i}^4 \right] + \dots$$
(5.23)

The order-parameter $\eta_{\iota_{\epsilon}i}$ responsible for the phase transition (with an associated expansion coefficient $A_{\iota_{\epsilon}}(T, P)$) may be singled out according to the following definition (Tolédano & Tolédano, 1987):-

- For $T > T_{cs}$ the coefficients $A_{\iota}(T, P_{cs})$ are positive.
- $A_{\iota_c}(T, P_{cs})$ vanishes for $T = T_{cs}$.
- In the neighbourhood of T_{cs} all coefficients $A_i(T, P_{cs})$ are strictly positive except for one $A_{\iota_c}(T, P_{cs})$ that vanishes with a change of sign at T_{cs} . Its temperature dependence close to T_{cs} is given by

$$A_{\iota_e} = A_{\iota_e}' \left(T - T_{cs} \right)$$

In the situation where other quantities η_{ii} also possess the property of being zero for $T \geq T_{cs}$ and non-zero for $T < T_{cs}$, but their associated coefficients $A_i(T, P_{cs})$ remain strictly positive in the neighbourhood of T_{cs} , such quantities are known as secondary order-parameters. In these situations the parameter η_{ici} will be referred to as the primary order-parameter.

In general there are two types of structural phase transitions in solids that are distinguished by the physical nature of their order-parameter; a *displacive* structural phase transition where the order-parameter represents a collective dispacement of the atoms (ions etc. ...) of the structure with respect to the average positions occupied (in equilibrium) in the high symmetry phase, and an *order-disorder* phase transition in which certain atoms of the crystal occupy several structural sites with equal probability in the high symmetry phase but below T_{cs} there is a spontaneous ordering of the atoms in one position.

Application of Landau theory to the possible structural phase transitions within a silicon 'poor' phase

As a brief reminder of the aim of this discussion, we have been considering a CeSi_x (1.80 $\leq x \leq \approx$ 1.90) sample which, at sufficiently high temperatures, is single phase and has the tetragonal ThSi₂-type crystal structure. At a critical temperature T_{cs} a phase separation occurs in CeSi_x. For $T < T_{cs}$ two phases coexist within the sample which have the same crystal structure as the high temperature phase but differ by their concentration of silicon atoms. Here, we consider the low temperature phase with the smaller concentration of silicon atoms, the silicon 'poor' phase (denoted as CeSi_y in equation (5.1)). Using the Landau theory of phase transitions, we consider the possible structural phase transitions that can occur within this phase as a result of an order-disorder transition and/or a displacive transition. In accordance with the experimental observations, the former will be an ordering of silicon vacancies and the latter will be an orthorhombic lattice distortion to the GdSi₂-type structure.

From the experimental observations, the starting point taken for this discussion is that the initial high symmetry phase has the ThSi₂-type structure and, following a structural phase transition, the final lower symmetry phase has the GdSi₂-type structure. In the situation where we are considering the structural phase transition to be an order-disorder type transition, the distortion of the lattice to the GdSi₂type structure is assumed to be extremely small but sufficient so as to produce two inequivalent types of silicon lattice sites within the crystal. The crystallographic space groups of the high and low symmetry phases surrounding the phase transition are respectively

$$G_0 = I4_1/amd, \qquad G_1 = Imma \tag{5.24}$$

Since G_1 is an equi-translational subgroup of G_0 and the number of atoms per unit cell remains unchanged within the two space groups, only the transformation properties of the possible order-parameters under the symmetry operations of the crystallographic point groups \tilde{G}_0 and \tilde{G}_1 need to be considered. The respective point groups are

$$\tilde{G}_0 = 4/mmm, \qquad \tilde{G}_1 = mmm$$
 (5.25)

It is noted that in using only \tilde{G}_0 and \tilde{G}_1 , the 4-fold screw axis of the space group G_0 is replaced by a 4-fold rotation axis and similarly the 2-fold screw axis of G_1 becomes a 2-fold rotation axis in \tilde{G}_1 .

The first step in the analysis of the possible phase transitions via the phenomenological theory is the construction of a thermodynamic potential \mathcal{G} that is invariant with respect to the symmetry operations of the high symmetry point group, \bar{G}_0 . The method of constructing basis functions ψ_i of a crystal point group irreducible representation (Γ_i) from physical quantities specifying the state of the crystal after a phase transition (i.e. from possible order-parameter components) relies on the use of projection operators. A projection operator \hat{P}_i is defined (Tolédano & Tolédano, 1987) by

$$\hat{P}_{\iota} = \frac{l_{\iota}}{d(\tilde{G}_0)} \sum_{\hat{g} \in \tilde{G}_0} \chi_{\iota}^*(\hat{g})\hat{g}$$
(5.26)

where l_{ι} is the dimensionality of the irreducible representation Γ_{ι} of \tilde{G}_{0} , $d(\tilde{G}_{0})$ is the number of symmetry elements $\hat{g} \in \tilde{G}_{0}$ and $\chi_{\iota}^{*}(\hat{g})$ is the complex conjugate of the character of the symmetry element \hat{g} within the representation Γ_{ι} . The action of the projection operator on an arbitrary function ψ from some space yields the function

$$\psi_{\iota} = \hat{P}_{\iota}\psi \tag{5.27}$$

Table 5.1: Projection of the strain tensor components $\epsilon_{\alpha\beta}$ onto the vector space of Γ_i of the crystallographic point group 4/mmm.

Γ	[e],
Г	$\frac{1}{1} \begin{pmatrix} \epsilon_{xx} + \epsilon_{yy} & 0 & 0 \\ 0 & \epsilon_{xx} + \epsilon_{yy} & 0 \end{pmatrix}$
~1	$\begin{pmatrix} 2 \\ 0 \\ 0 \\ 0 \\ 0 \\ 2\epsilon_{zz} \end{pmatrix}$
Γ_2	$ \left(\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
Γ_3	$\frac{1}{2} \begin{pmatrix} \epsilon_{xx} - \epsilon_{yy} & 0 & 0 \\ 0 & -\epsilon_{xx} + \epsilon_{yy} & 0 \\ 0 & 0 & 0 \end{pmatrix}$
Γ_4	$ \left(\begin{array}{cccc} 0 & \epsilon_{xy} & 0 \\ \epsilon_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{array}\right) $
Γ_5	$\begin{pmatrix} 0 & 0 & \epsilon_{xz} \\ 0 & 0 & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & 0 \end{pmatrix}$

which transforms according to the irreducible representation Γ_{ι} of the group G_0 . Accordingly, if the function ψ does not have the symmetry of Γ_{ι} then the projection $\psi_{\iota} = 0$. The choice of the arbitrary trial function ψ is discussed below.

There are several material tensors that may be used to specify the various properties of crystals and hence the occurrence of spontaneous physical quantities at a phase transition, e.g. polarization, magnetization, stress, susceptibility, etc. ... (Izyumov & Syromyatnikov, 1990). Here, to consider the possibility of a displacive phase transition within a CeSi_y silicon 'poor' phase, the strain tensor [ϵ] (with symmetric components $\epsilon_{\alpha\beta}$) will be the most appropriate. Using (5.26), (5.27) and the character tables of the crystallographic point group irreducible representations (Koster *et al.*, 1963), the projections of the strain tensor onto the spaces associated with the irreducible representations Γ_{ϵ} of \tilde{G}_{0} have been calculated. The explicit calculations are given in

Table 5.2: Projection of the 'disorder' parameter Δ and the 'total-probability' parameter N onto the spaces associated with the irreducible representations Γ , of the crystallographic point group 4/mmm.

Γ	n_1^ι	n_2^{ι}	N,	Δ
Γ1	$\frac{1}{2}(n_1+n_2)$	$\frac{1}{2}(n_2+n_1)$	$n_1 + n_2$	0
Γ_2	0	0	0	0
Γ_3	$rac{1}{2}(n_1-n_2)$	$rac{1}{2}(n_2-n_1)$	0	$n_1 - n_2$
Γ_4	0	0	0	0
Γ_5	0	0	0	0

Appendix A and the results shown in Table 5.1. They are in agreement with those listed in Izyumov & Syromyatnikov (1990) and Janovec et al. (1975).

In an order-disorder type phase transition the order-parameter consists of the difference between the probabilities of occupation of two lattice sites that are equivalent in the high symmetry phase above T_{cs} . For the phase transition within the CeSi_y phase we define such an order-parameter by

$$\Delta = n_1 - n_2 \tag{5.28}$$

where n_1 and n_2 are the probabilities of occupation of the two inequivalent silicon lattice sites within the GdSi₂-type structure. The projection of Δ onto the space associated with the ι^{th} irreducible representation Γ_{ι} is given by

$$\Delta_{\iota} = n_1^{\iota} - n_2^{\iota} \tag{5.29}$$

where n_i^{ι} (i = 1, 2) is the corresponding projection of the probability n_i onto the space associated with Γ_{ι} . In a similar manner, a 'total-probability' parameter N may be defined and its associated projection N_{ι} given by

$$N_{\iota} = n_1^{\iota} + n_2^{\iota} \tag{5.30}$$

The projections of Δ and N onto the spaces associated with the irreducible representations Γ_{ι} of \tilde{G}_0 have been calculated explicitly in Appendix A and the results are shown in Table 5.2. Using the results of Tables 5.1 and 5.2, it is possible now to construct expansions of the Gibbs free energy of a CeSi_y silicon 'poor' phase, in terms of the possible order-parameters, that are invariant with respect to the symmetry operations of the crystallographic point group $\tilde{G}_0 = 4/mmm$. Such expansions are performed below for each of the three possible types of structural phase transitions that may occur within CeSi_y, i.e. for a displacive structural phase transition, for an order-disorder phase transition and finally for a phase transition in which both of the former processes occur. In accordance with Tolédano & Tolédano (1987), the latter type of structural phase transition in CeSi_y is known as a *proper-ferroelastic* phase transition.

Displacive structural phase transition

For a displacive structural phase transition in the CeSi_v system which changes from a high symmetry ThSi₂-type structure to a lower symmetry GdSi₂-type structure, it is evident from Table 5.1 that only the combination of components of the spontaneous strain tensor (and which transform according to the irreducible representation Γ_3 of \tilde{G}_0) may be considered as the order-parameter characterizing such a phase transition. The Landau condition (5.21) necessarily enforces the absence of the components $[\epsilon]_1$. For convenience the symbol v will be used to denote such an order-parameter,

$$\upsilon = \frac{1}{2} \left(\epsilon_{xx} - \epsilon_{yy} \right) \tag{5.31}$$

Performing a fourth-order expansion of the free energy in terms of the order-parameter v (and ensuring that each contribution is invariant with respect to the symmetry operations of the point group \tilde{G}_0) then

$$\mathcal{G}(T, P, \upsilon) = \mathcal{G}_0(T, P) + \frac{1}{2}a_1\upsilon^2 + \frac{1}{4}a_2\upsilon^4 + \dots$$
 (5.32)

The representation multiplication tables for the IR's of G_0 (Koster *et al.*, 1963) show that there can be no linear or third order terms in this expansion. The coefficients a_1 and a_2 are functions of T and P. For a stable equilibrium it is required that

$$\frac{\partial \mathcal{G}}{\partial v} = 0 \qquad \Rightarrow \qquad v\left(a_1 + a_2 v^2\right) = 0 \tag{5.33}$$

and

$$\frac{\partial^2 \mathcal{G}}{\partial v^2} > 0 \qquad \Rightarrow \qquad a_1 + 3a_2 v^2 > 0 \tag{5.34}$$

At high temperatures $(T > T_{cs})$ the equilibrium conditions require that both of the coefficients a_1 and a_2 are positive and the stable equilibrium is given by v = 0. At T_{cs} the coefficient a_1 must vanish and become negative for $(T < T_{cs})$ such that the condition $v \neq 0$ (required by definition of the order-parameter) is compatible with the minimum of the free energy below T_{cs} . It is assumed that the coefficient a_1 may be expanded as a function of T in terms of

$$a_1 = a_1' \left(T - T_{cs} \right) \tag{5.35}$$

Thus for temperatures $T < T_{cs}$, (5.33) has a stable solution for

$$v = \pm \sqrt{\frac{a_1'(T_{cs} - T)}{a_2}}$$
(5.36)

The order-parameter v is zero at T_{cs} and changes continuously with temperature below T_{cs} . Correspondingly, the entropy of the system is given by

$$S = -\frac{\partial \mathcal{G}}{\partial T} \tag{5.37}$$

Using (5.32) and ignoring fourth-order and higher terms in v then

$$S = S_0 - \frac{1}{2} \frac{\partial a_1}{\partial T} v^2 \tag{5.38}$$

since the term containing the temperature derivative of v is zero as $\frac{\partial g}{\partial v} = 0$. Thus for temperatures above T_{cs} , v = 0 and $S = S_0$, and for $T < T_{cs}$

$$S = S_0 + \frac{a_1^{\prime 2}}{2a_2} \left(T - T_{cs} \right) \tag{5.39}$$

Hence, due to the continuous nature of the coefficients a_1 and a_2 , the variation of the entropy at T_{cs} is continuous and the phase transition is of second-order.

Order-disorder phase transition

From Table 5.2, only the components of the disorder parameter transforming according to the irreducible representation Γ_3 of \tilde{G}_0 may be the possible order-parameter characterizing an order-disorder phase transition in CeSi_y. For the total-probability parameter N, the projection $N_1 = n_1 + n_2$ is a constant and as such may not be used as a variational parameter. For the disorder parameter $\Delta = n_1 - n_2$, the Taylor series expansion of the free energy that is invariant with respect to the symmetry operations of $ilde{G}_0$ is given by

$$\mathcal{G}(T, P, \Delta) = \mathcal{G}_0(T, P) + \frac{1}{2}b_1\Delta^2 + \frac{1}{4}b_2\Delta^4 + \dots$$
 (5.40)

The Γ_3 symmetry of the order-parameter restricts that there are no linear or thirdorder terms in (5.40). The conditions for a stable equilibrium phase below T_{cs} require that

$$\frac{\partial \mathcal{G}}{\partial \Delta} = 0 \qquad \Rightarrow \qquad \Delta \left(b_1 + b_2 \Delta^2 \right) = 0 \tag{5.41}$$

and

$$\frac{\partial^2 \mathcal{G}}{\partial \Delta^2} > 0 \qquad \Rightarrow \qquad b_1 + 3b_2 \Delta^2 > 0 \tag{5.42}$$

Again the solution to equations (5.41) and (5.42) requires that for $T > T_{cs}$ the coefficients b_1 and b_2 are positive and $\Delta = 0$. In a similar manner to the previous discussion, the coefficient b_1 related to the order-parameter is considered to have a linear temperature dependence in the vicinity of T_{cs} and for temperatures $T < T_{cs}$ the stable equilibrium conditions give that

$$\Delta = \pm \sqrt{\frac{b_1' \left(T_{cs} - T \right)}{b_2}}$$
(5.43)

There exists a continuous second-order phase transition at T_{cs} .

Proper-ferroelastic phase transition

It is often observed experimentally that when a primary order-parameter is of the order-disorder type, a secondary order-parameter of the displacive type will often exist, e.g. a symmetry-breaking strain (Tolédano & Tolédano, 1987). The consequences of such a structural phase transition in which both processes occur will be discussed here.

The preceeding discussions have shown that both the v and Δ order-parameters that may be used to characterize the structural phase transitions of CeSi_y transform under the symmetry operations of \tilde{G}_0 according to the same irreducible representation, Γ_3 . Hence, an expansion of the free energy that remains invariant under the symmetry operations of the group \tilde{G}_0 may only contain terms with even powers of the order-parameter components. However, in this situation it is possible to have a linear coupling term between the order-parameters v and Δ , such that the invariant expansion is given by

$$\mathcal{G}(T, P, v, \Delta) = \mathcal{G}_0(T, P) + \frac{1}{2}a_1v^2 + \frac{1}{4}a_2v^4 + \frac{1}{2}b_1\Delta^2 + \frac{1}{4}b_2\Delta_1^4 + cv\Delta + \dots \quad (5.44)$$

where all the coefficients a_1 , a_2 , b_1 , b_2 , c, ..., are functions of T and P.

The conditions for the existence of stable equilibrium phases below T_{cs} are given by

$$\frac{\partial \mathcal{G}}{\partial \upsilon} = 0 \qquad \Rightarrow a_1 \upsilon + a_2 \upsilon^3 + c\Delta = 0 \tag{5.45}$$

$$\frac{\partial \mathcal{G}}{\partial \Delta} = 0 \qquad \Rightarrow b_1 \Delta + b_2 \Delta^3 + c\upsilon = 0 \tag{5.46}$$

$$\frac{\partial^2 \mathcal{G}}{\partial v^2} > 0 \qquad \Rightarrow a_1 + 3a_2v^2 > 0 \tag{5.47}$$

$$\frac{\partial^2 \mathcal{G}}{\partial \Delta^2} > 0 \qquad \Rightarrow b_1 + 3b_2 \Delta^2 > 0 \tag{5.48}$$

and

$$\frac{\partial^2 \mathcal{G}}{\partial v \partial \Delta} > 0 \quad , \quad \frac{\partial^2 \mathcal{G}}{\partial \Delta \partial v} > 0 \qquad \Rightarrow c > 0 \tag{5.49}$$

For the situation where c = o, there is no coupling term between the order-parameters v and Δ and equations (5.45) and (5.46) have solutions

$$v = 0$$
 $(T \ge T_{cs}),$ $v = \pm \sqrt{\frac{a_1'(T_{cs} - T)}{a_2}}$ $(T < T_{cs})$ (5.50)

and

$$\Delta = 0 \qquad (T \ge T_{cs}), \qquad \Delta = \pm \sqrt{\frac{b_1'(T_{cs} - T)}{b_2}} \qquad (T < T_{cs}) \qquad (5.51)$$

respectively. In either case there is a continuous second-order phase transition at T_{cs} .

For the situation where $c \neq 0$, the first case that will be considered is where Δ is the primary order-parameter responsible for the phase transition and v the secondary order-parameter. For temperatures $T > T_{cs}$, the conditions (5.45) to (5.49) for the existence of a stable equilibrium require that $v = \Delta = 0$ and all of the coefficients a_1 , a_2 , b_1 , b_2 and c are positive. In the vicinity of T_{cs} only the coefficient b_1 relating to the primary order-parameter will vanish and become negative below T_{cs} (see discussion, p. 111) whilst the remaining coefficients remain strictly positive.

Making the assumption that just below T_{cs} the secondary order-parameter v is small and third-order terms in (5.45) may be neglected, then

$$v \approx -\frac{c}{a_1} \Delta \tag{5.52}$$

and substituting for v in (5.46) gives

$$b_1'(T - T_{cs})\Delta + b_2\Delta^3 + c\left(-\frac{c}{a_1}\Delta\right) = 0$$

$$\Rightarrow \Delta \left[a_1b_1'(T - T_{cs}) - c^2 + a_1b_2\Delta^2\right] = 0$$
(5.53)

The solutions to (5.53) are given by

$$\Delta = 0 \qquad (T \ge T_{cs})$$

$$a_1 b'_1 (T - T_{cs}) - c^2 + a_1 b_2 \Delta^2 = 0 \qquad (T < T_{cs}) \qquad (5.54)$$

Thus for $T < T_{cs}$,

$$\Rightarrow \Delta = \pm \sqrt{\frac{c^2 + a_1 b_1' (T_{cs} - T)}{a_1 b_2}} \tag{5.55}$$

at T_{cs} where $b'_1 = 0$,

$$\Delta = \pm \sqrt{\frac{c^2}{a_1 b_2}} \tag{5.56}$$

and it may be seen from (5.54) that now the condition

$$c^{2} - a_{1}b'_{1}(T - T_{cs}) = 0 \qquad (T = T'_{cs}) \qquad (5.57)$$

is required for $\Delta = 0$. Thus the effect of the coupling is to renormalize the transition temperature T_{cs} to T'_{cs} .

Substituting (5.52) into (5.44) and ignoring fourth-order and higher terms in Δ then

$$\mathcal{G} = \mathcal{G}_0 + \frac{1}{2} \left[b_1'(T - T_{cs}) - \frac{c^2}{a_1} \right] \Delta^2$$
(5.58)

and the entropy of the system is given by

$$S = S_0 + \frac{\Delta^2}{2} \left[\frac{1}{a_1} \frac{\partial}{\partial T} c^2 - \frac{c^2}{a_1^2} \frac{\partial}{\partial T} a_1 - \frac{\partial}{\partial T} b_1' \left(T - T_{cs}\right) \right]$$
(5.59)

Due to the continuous nature of all of the coefficients the variation of S will be continuous and there will be a second-order phase transition at the transition temperature T'_{cs} , determined by the condition (5.57). In exactly the same manner as above, for the situation where v is considered to be the primary order-parameter responsible for the phase transition and Δ the secondary order-parameter, the phase transition will be of second-order. In conclusion, for a structural phase transition in a CeSi_y silicon 'poor' phase in which there is both a silicon vacancy ordering and an orthorhombic distortion below T_{cs} , Landau theory predicts that the phase transition will be of second-order and that the only effect of the coupling will be to renormalize the phase transition temperature.

5.2 Magnetic phase transitions in $CeSi_x$

In view of the observations from the neutron diffraction experiments described in § 3.3, § 3.6 and § 4.3, the proposed magnetic phase diagram of CeSi_x (1.60 $\leq x \leq$ 2.00), both as a function of temperature and silicon concentration, is illustrated schematically in Fig. 5.3. Only CeSi_x ($x \leq x_c \approx 1.80$) samples with the orthorhombic GdSi_2 type structure are observed to have magnetically ordered ground states. The Curie temperature ranges between 10 \rightarrow 13K for CeSi_x ($x = 1.60 \rightarrow 1.80$). For CeSi_{1.70}, the ferromagnetically ordered moments lie mainly in the a-b plane ($\approx 0.45 \ \mu_B/\text{Ce}$) with only a small ordered component (< 0.07 μ_B/Ce) along the c-axis. Thus far, the existence of a second magnetic phase transition $(T_N \approx 12 \text{K})$ has been observed in CeSi_{1.70} and CeSi_{1.75} samples and for CeSi_{1.70}, the magnetic order has been identified as a weak antiferromagnetic modulation superposed onto the ferromagnetically ordered moments, the period of which is the same as that of the chemical unit cell along the c-axis. For the CeSi_x (1.80 $\leq x \leq 2.00$) samples that have no magnetically ordered ground state, in a CeSi_{1.85} sample that remains paramagnetic down to at least 2K, the existence of antiferromagnetic correlations have been observed, the magnitude of which increase with increasing temperature.

In the following discussion, only the temperature dependent magnetic phase transitions in CeSi_x ($x \leq 1.80$) samples will be considered. In accordance with the experimental observations on CeSi_{1.80} (NF) (§ 3.3), it is assumed that all such samples are single phase and retain the GdSi₂-type crystal structure both above and below the magnetic transition temperature. Below, the essential features of the Landau theory of magnetic systems are reviewed and subsequently, the Landau theory is



Figure 5.3: Schematic illustration of the proposed magnetic phase diagram for CeSi_x (1.60 $\leq x \leq 2.00$).

used to discuss the possible types of magnetic ordering that can occur within CeSi_x ($x \leq 1.80$) samples, subject to the symmetry constraints.

Introduction to Landau theory for magnetic systems

In the description of a magnetic system it is the electric current density that is used to account for the distribution of moving electric charges within the system. The magnetic symmetry of a crystal is given by the group of symmetry operations that leave invariant the mean electric current density, j(r). The group is obtained by combining the rotations, reflections and translations of the crystallographic space group G with the time-inversion operator $\hat{\Theta}$. For example, a paramagnetic crystal is described by a Type II Shubnikov magnetic space group \mathcal{M} , given by

$$\mathcal{M} = G + \hat{\Theta}G \tag{5.60}$$

For a thorough description of the different types of magnetic groups and their construction, the reader is referred to Bradley & Cracknell (1972) or Joshua (1991). Both of these texts also give an excellent description of the application of group theory to magnetic groups, known as *Corepresentation theory*. In the following discussion the notation of Bradley & Cracknell is used, unless stated otherwise.

In Landau theory, a phase transition from a paramagnetic to a magnetically ordered phase is characterized by the onset of a non-zero average density of the magnetic moment $\mu(r)$ below the transition temperature T_c , where

$$\mu(\mathbf{r}) = \int \mathbf{r} \times \mathbf{j}(\mathbf{r}) d^3 \mathbf{r}$$
 (5.61)

In accordance with a second-order phase transiton, $\mu(r)$ changes continuously across the transition point. It is considered that $\mu(r) = 0$ at T_c and is small at temperatures near T_c and as such, the free energy \mathcal{G} of the system may be expanded in powers of $\mu(r)$. The cartesian components $\mu_i(r)$ (i = x, y, z) are expanded within a basis ϕ_{α}^i that spans the ι^{th} irreducible corepresentation (IC) of the symmetry group \mathcal{M} that describes the high temperature, high symmetry phase, i.e.

$$\mu_i(r) = \sum_{\iota,\alpha} N^{\iota}_{i\alpha} \phi^{\iota}_{\alpha}(r)$$
(5.62)

where the subscript α denotes the functions belonging to the IC $D\Gamma_{\iota}$. It is assumed that in a transformation of the coordinates x, y, z, the functions $\phi_{i\alpha}^{\iota}(r)$ remain fixed and the $N_{i\alpha}^{\iota}$ transform as the direct product of the ι^{th} IC of the paramagnetic group and of the axial vectorial representation of this group. Thus the corepresentation spanning the $N_{i\alpha}^{\iota}$ is reducible.

Similar to § 5.1, the free energy \mathcal{G} is expanded in powers of the $N_{i\alpha}^{*}$ such that the expansion remains invariant under the symmetry operations of the paramagnetic group \mathcal{M} . As the time-inversion operator is itself a symmetry operation of the group \mathcal{M} (since $\hat{\Theta}\hat{E} = \hat{\Theta}$), no odd terms may be present in the expansion of \mathcal{G} since $\hat{\Theta}$ changes the sign of all of them. Despite the fact that the $N_{i\alpha}^{*}$ transform as a reducible corepresentation, it is considered to be more convenient to use such terms in the expansion of \mathcal{G} rather than linear combinations of the $N_{i\alpha}^{*}$ that transform as irreducible corepresentations. This is because the former method allows the separation, within the Landau expansion of the free energy, of the isotropic invariants (which originate from exchange forces) from anisotropic invariants (associated with relativistic effects) arising from spin-spin and spin-orbit interactions, and thus permits an estimate of the relative order of magnitude of the corresponding coefficients. To determine which combinations of terms $N_{i\alpha}^{*}$ are permissible in the expansion of \mathcal{G} , for the anisotropic terms the projection operator technique is employed. For the isotropic terms, it is recalled that the magnitude of such exchange forces is invariant with respect to a rotation of the spins by the same arbitrary angle, thus the exchange force invariants are given by combinations of the $N_{i\alpha}^{t}$ that do not change under rotation by an arbitrary angle with respect to the index *i* and for a given α . As shown above, no odd terms may be present in the expansion of \mathcal{G} and thus only scalar products of the type

$$N_{i\alpha}^{\iota}.N_{j\beta}^{\xi} \tag{5.63}$$

are permissible, where ι and ξ are IC's of the group \mathcal{M} , (i, j = x, y, z) and α and β denote the different functions belonging to the respective IC. As the products (5.63) tranform according to the direct products of the IC's ι and ξ , the antiunitary nature of the IC's gives that

$$N_{i\alpha}^{\iota} N_{j\beta}^{\xi} = C \delta_{\iota\xi} \delta_{ij} \delta_{\alpha\beta} \tag{5.64}$$

where C is a constant and the δ 's are Kronecker products. The relation (5.64) expresses an orthogonality property, i.e. different vectors $N_{i\alpha}^{t}$ are perpendicular to each other. The maximum number of non-vanishing vectors $N_{i\alpha}^{t}$ corresponds to the dimensionality of the reducible corepresentation involved in the transition.

The expansion of \mathcal{G} is given by

$$\mathcal{G} = \mathcal{G}_0 + \sum_{\iota} a^{\iota} \sum_{i,\alpha} \left(N_{i\alpha}^{\iota} \right)^2 + \dots$$
 (5.65)

where the a^{t} are coefficients which depend on T and P. It can be seen from (5.65) that the high temperature, high symmetry paramagnetic state corresponds to all $N_{i\alpha}^{t} = 0$ which can only take place when all $a^{t}(T, P) > 0$. Non-zero $N_{i\alpha}^{t}$ appear if one (and only one) of the coefficients a^{t} changes sign. In the Landau formulation, the $N_{i\alpha}^{t}$ are determined from the minimization of (5.65) and then are used in (5.62) to determine the equilibrium magnetic moment density, i.e. the magnetic structure of the crystal. The minimization of \mathcal{G} is performed in two steps:-

- 1. A minimization of the exchange part of \mathcal{G} which gives the angles between the magnetic moments located at the different magnetic atoms.
- 2. A minimization of the anisotropic part of \mathcal{G} which provides the orientation of the N^{ι}_{α} relative to the crystallographic axes.

Transition from a paramagnetic to a magnetically ordered phase within orthorhombic $CeSi_x$

This discussion considers a transition from a paramagnetic to a magnetically ordered state in $\operatorname{CeSi}_x (x \leq x_c \approx 1.80)$ as a function of temperature. Via the application of Landau theory, the possible types of ordering of the magnetic moments in CeSi_x are determined, as described below.

Both the high and low temperature CeSi_x phases have the orthorhombic GdSi_2 type crystal structure and thus the crystallographic space group *Imma*. Accordingly, the starting point taken for this discussion is

$$G_0 = G_1 = Imma \tag{5.66}$$

and thus the corresponding point groups are

$$\tilde{G}_0 = \tilde{G}_1 = mmm \tag{5.67}$$

Since the number of atoms in the elementary unit cell remains unchanged across the transition, the wave vector of the paramagnetic Brillouin zone associated with the transiton is k=0 and thus is located at the Γ point of the primitive orthorhombic magnetic Brillouin zone. The high temperature, high symmetry paramagnetic phase is described by a Type II Shubnikov magnetic space group, \mathcal{M} , given by

$$\mathcal{M} = G_0 + \hat{\Theta}G_0 \tag{5.68}$$

Since the translation symmetry operations of the high and low symmetry space groups are identical, i.e. k=0, it will be sufficient to consider only the symmetry operations of the magnetic point group, $\tilde{\mathcal{M}}$, where

$$\tilde{\mathcal{M}} = \tilde{G}_0 + \hat{\Theta}\tilde{G}_0 \tag{5.69}$$

Following the notation of Bradley & Cracknell (1972) then from (5.66) and (5.67) the magnetic groups are respectively

$$\mathcal{M} = Immal' \tag{5.70}$$

$$\tilde{\mathcal{M}} = mmm1' \tag{5.71}$$

The superscript / denotes the coloured symmetry elements within the group.

In order to specify the possible sublattice arrangements of the magnetic moments of the ordered phase, it is necessary to take into consideration both the exchange and spin-spin, spin-orbit interaction energies. Whereas the former determines the angles between the moments located on different magnetic atoms and thus the nature of the magnetic ordering, the latter interactions are of relativistic origin and they determine the actual orientation of the magnetic moments relative to the crystallographic axes. The elementary unit cell of $CeSi_x$ with the orthorhombic $GdSi_2$ -type structure contains four cerium atoms in special positions, as shown in Fig. 5.4. Momentarily taking into consideration only the exchange forces then, below T_c , the possible relative ordering of the magnetic moments on each of the four cerium ions that is associated with the symmetries of the IC's of the paramagnetic group mmml' (i.e. Immal' at k=0) may be determined. The calculations are performed in Appendix B and the configurations are illustrated in Fig. 5.5. However, to determine the exact nature of the possible magnetic order below T_c , it is necessary to determine the transformation properties of the $N_{i\alpha}^{\iota}$ in (5.62) so that a Landau expansion of the free energy in terms of both exchange and relativistic energies may be constructed. A minimization of the free energy thus determines the actual sublattice ordering, as calculated below for CeSi_{x} .

Nature of the magnetic order below T_c

Associating a magnetic moment μ^{j} (j = 1, ..., 4) to each of the inequivalent cerium ions within the *Imma* unit cell (illustrated in Fig. 5.4), then for the four types of sublattices illustrated in Fig. 5.5 it is possible to define the following vectors

$$M = \mu^{1} + \mu^{2} + \mu^{3} + \mu^{4}$$

$$L_{1} = \mu^{1} - \mu^{2} + \mu^{3} - \mu^{4}$$

$$L_{2} = \mu^{1} - \mu^{2} - \mu^{3} + \mu^{4}$$

$$L_{3} = \mu^{1} + \mu^{2} - \mu^{3} - \mu^{4}$$
(5.72)

that represent respectively the total magnetization of a unit cell and the three possible antiferromagnetic collinear lattices. For the one-dimensional IC's of the paramagnetic



Figure 5.4: The cerium sublattice of CeSi_x with the GdSi_2 -type structure (space group *Imma*). In relation to the atomic positions listed in the International Tables of Crystallography (Hahn, 1983) the figure has been drawn with the unit cell translated by $(0, \frac{1}{2}, z \approx 0.377)$, such that this different sublattice has a cerium atom at the origin. The labelling denotes the four special positions of the cerium atoms in the lattice.



Figure 5.5: The possible magnetic ordering induced within a crystallographic unit cell of CeSi_x by the irreducible correpresentations $\mathcal{D}\Gamma_i^-$ ($\iota = 1, \ldots, 4$) of the magnetic group mmm1', assuming the magnetic moments orientate along the z-axis.

group $\tilde{\mathcal{M}} = mmm1'$ there will only be one component α in the expansion (5.62) of μ that needs to be considered, thus

$$\mu_i(\mathbf{r}) = N_i^\iota \phi^\iota(\mathbf{r}) \tag{5.73}$$

where each component μ_i (i = x, y, z) transforms as the direct product of the ι^{th} IC of the group $\tilde{\mathcal{M}}$ and the axial vectorial representation of this group. Taking into account the transformation of the atoms $1 \rightarrow 4$ under the symmetry operations of the crystal point group mmm (listed in Table 5.3), the transformation properties of the vectors M and L_β $(\beta = 1, 2, 3)$ under the symmetry operations of the magnetic point group mmm1' may be determined. They are shown in Table 5.4. However, to determine the components M_i and $L_{\beta i}$ that are associated with each one of the four IC's of mmm1', it is necessary to combine the transformation properties shown in Table 5.4 with the transformation of the space coordinates of the components μ_i (i = x, y, z)under the symmetry operations of the point group mmm, shown in Table 5.5. Using the projection operator technique, such a calculation has been performed explicitly in Appendix B and the results are shown in Table 5.6.

The results of Table 5.6 allow the Landau expansion of the free energy to be constructed in terms of the components M_i and $L_{\beta i}$ $(i = x, y, z, \beta = 1, 2, 3)$. Since the ratio of the magnetic anisotropy energy to the exchange energy (and the ratio of their corresponding coefficients in the Landau expansion) lies in the range $10^{-3} \rightarrow 10^{-5}$ (Tolédano & Tolédano, 1987), within the expansion the exchange terms are written up to fourth degree whereas the relativistic terms are taken to second degree. The expansion of \mathcal{G} that is invariant with respect to the symmetry operations of the paramagnetic group $\tilde{\mathcal{M}} = mmm1'$ is given by

$$\mathcal{G} = \mathcal{G}_{0} + \sum_{\beta} \frac{a_{\beta}}{2} L_{\beta}^{2} + \frac{c}{2} M^{2} + \sum_{\beta} \frac{b_{\beta}}{4} L_{\beta}^{4} + \frac{d}{4} M^{4} + \frac{1}{2} \sum_{\beta,i} \left(\nu_{\beta i} L_{\beta i}^{2} + \xi_{i} M_{i}^{2} \right) + \delta_{x} L_{3x} M_{x} + \delta_{y} L_{3y} M_{y} + \delta_{z} L_{3z} M_{z}$$
(5.74)

From (5.74) it is now possible to discuss, in a complete manner, the type and nature of the magnetic order that can occur in CeSi_x below T_c .

Table 5.3: Transformation of cerium atom positions $1 \rightarrow 4$ in the unit cell of CeSi_x under the symmetry operations of the point group *mmm*.

cerium atom position	Ê	\hat{C}_{2z}	\hat{C}_{2y}	\hat{C}_{2x}	Î	σ ,	σy	$\hat{\sigma}_{x}$
1	1	1	2	2	2	2	1	1
2	2	2	1	1	1	1	2	2
3	3	3	4	4	4	4	3	3
4	4	4	3	3	3	3	4	4

Table 5.4: Transformation properties of the vectors M and L_{β} ($\beta = 1, 2, 3$) under the symmetry operations of the magnetic point group mmm1'.

vector	Ê	\hat{C}_{2z}	\hat{C}_{2y}	\hat{C}_{2x}	Î	$\hat{\sigma}_{z}$	$\hat{\sigma}_{y}$	$\hat{\sigma}_{x}$
M	M	M	M	M	M	M	M	M
L_1	L_1	L_1	$-L_1$	- L_1	$-L_1$	$-L_1$	L_1	L_1
L_2	L_2	L_2	$-L_2$	$-L_2$	$-L_2$	$-L_2$	L_2	L_2
L_3	L_3	L_3	L_3	L_3	L_3	L_3	L_3	L_3
vector	ΘÊ	$\hat{\Theta}\hat{C}_{2z}$	$\hat{\Theta}\hat{C}_{2y}$	$\hat{\Theta}\hat{C}_{2x}$	ΘÎ	Ôô,	$\hat{\Theta}\hat{\sigma}_y$	$\hat{\Theta}\hat{\sigma}_{x}$
M	-M	-M	- <i>M</i>	-M	- <i>M</i>	- <i>M</i>	-M	-M
L_1	$-L_1$	$-L_1$	L_1	L_1	L_1	L_1	$-L_1$	$-L_1$
L_2	-L2	$-L_2$	L_2	L_2	L_2	L_2	$-L_2$	$-L_2$
L_3	- <i>L</i> 3	- L_3	- L_3	$-L_3$	$-L_3$	$-L_3$	- L_3	- L_3

Table 5.5: Transformation properties of the magnetic moment components μ_i (i = x, y, z) under the symmetry operations of the crystallographic point group mmm.

component	Ê	\hat{C}_{2z}	\hat{C}_{2y}	\hat{C}_{2x}	Î	σ ,	$\hat{\sigma}_{\mathbf{y}}$	$\hat{\sigma}_{x}$
μ_x	μ_x	$-\mu_{x}$	$-\mu_x$	μ_x	μ_x	$-\mu_x$	$-\mu_{x}$	μ_x
μ_y	μ_y	$-\mu_{y}$	μ_y	$-\mu_y$	$\mu_{m y}$	$-\mu_y$	μ_y	$-\mu_y$
μ_z	μ_z	μ_z	$-\mu_z$	$-\mu_z$	μ_{z}	μ_{z}	$-\mu_z$	$-\mu_z$

Table 5.6: The components of the vectors M and L_{β} ($\beta = 1, 2, 3$) that form a basis for the irreducible corepresentations of *Immal'* at k=0.

IC	Components
$\mathcal{D}\Gamma_{1}^{-}$	0
$\mathcal{D}\Gamma_2^-$	$M_{oldsymbol{y}}$, $L_{3oldsymbol{y}}$
$\mathcal{D}\Gamma_{3}^{-}$	M_z , L_{3z}
$\mathcal{D}\Gamma_4^-$	M_x , L_{3x}

For a first approximation to the magnetic order in CeSi_x , the relativistic terms in (5.74) are neglected, leaving explicitly

$$\mathcal{G} = \mathcal{G}_0 + \frac{a_1}{2}L_1^2 + \frac{a_2}{2}L_2^2 + \frac{a_3}{2}L_3^2 + \frac{c}{2}M^2 + \frac{b_1}{4}L_1^4 + \frac{b_2}{4}L_2^4 + \frac{b_3}{4}L_3^4 + \frac{d}{4}M^4$$
(5.75)

The stable equilibrium state of the ordered moments is determined by

$$\sum_{\beta} \frac{\partial \mathcal{G}}{\partial L_{\beta}} = 0, \qquad \Rightarrow \sum_{\beta} L_{\beta} \left(a_{\beta} + b_{\beta} L_{\beta}^{2} \right) = 0$$
$$\frac{\partial \mathcal{G}}{\partial M} = 0, \qquad \Rightarrow M \left(c + dM^{2} \right) = 0 \qquad (5.76)$$

$$\sum_{\beta} \frac{\partial^2 \mathcal{G}}{\partial L_{\beta}^2} > 0, \qquad \Rightarrow \sum_{\beta} a_{\beta} + 3b_{\beta}L^2 > 0$$
$$\frac{\partial^2 \mathcal{G}}{\partial M^2} > 0, \qquad \Rightarrow c + 3dM^2 > 0 \qquad (5.77)$$

Conditions (5.76) and (5.77) give that $a_{\beta} > 0$ ($\beta = 1, 2, 3$), c > 0 and the equilibrium values of the magnetizations within the unit cell are $|L_1| = |L_2| = |L_3| = |M| = 0$. These solutions correspond to the high temperature paramagnetic state. In accordance with the formulation of the Landau theory it is assumed that one of the a_{β} or c become zero at $T = T_c$ whilst the other coefficients remain positive. Since the dominant magnetic order in CeSi_x is known to be ferromagnetic in nature (§ 3.3 and § 4.3), it is taken that it is the coefficient c that becomes zero at $T = T_c$. Thus the equilibrium values for the lattice magnetizations are $|L_1| = |L_2| = |L_3| = 0$ and substitution into equations (5.72) gives

$$\mu^1 = \mu^2 = \mu^3 = \mu^4 \tag{5.78}$$

and the expected ferromagnetic order. From (5.76), the temperature dependence of the lattice magnetization is given by

$$|M| = \pm \sqrt{\frac{c(T_c - T)}{d}} \tag{5.79}$$

Taking the complete form of (5.74) into consideration but retaining the assumption that it is the coefficient c that vanishes first at T_c , the expansion of \mathcal{G} may be simplified by taking into consideration only invariants associated with the M_i components:

$$\mathcal{G} = \mathcal{G}_{0} + \frac{c}{2}M^{2} + \frac{d}{4}M^{4} + \frac{\xi_{x}}{2}M_{x}^{2} + \frac{\xi_{y}}{2}M_{y}^{2} + \frac{\xi_{z}}{2}M_{z}^{2} + \delta_{x}L_{3x}M_{x} + \delta_{y}L_{3y}M_{y} + \delta_{z}L_{3z}M_{z}$$
(5.80)

Minimization of (5.80) with respect to M_x gives

$$cM_x + dM_x^3 + \xi_x M_x + \delta_x L_{3x} = 0 \tag{5.81}$$

and close to below T_c , M_x is small and thus the exchange d term may be neglected with respect to the exchange c term and

$$L_{3x} \approx -\frac{(c+\xi_x)}{\delta_x} M_x \tag{5.82}$$

Performing similar minimizations of the free energy (5.80) with respect to M_y and M_z , it is clear that any component of ferromagnetic order within CeSi_x has the possibility of inducing a weak antiferromagnetic order parallel to the ferromagnetic component; i.e. for (i = x, y, z)

$$L_{3i} \approx -\frac{(c+\xi_i)}{\delta_i} M_i \tag{5.83}$$

Since the magnetic phase transition is associated with the wave vector k = 0, whereby the magnetic unit cell of the ordered phase is identical to the crystallographic unit cell of the paramagnetic phase, the antiferromagnetic scattering intensity will be found at the positions of the magnetic Bragg peaks and will result in a weak modulation of the ferromagnetic scattering intensity. This may be observed by substituting the relations $|L_1| = |L_2| = 0$ and those given by (5.83) into (5.72):-

$$\mu_i^1 + \mu_i^2 + \mu_i^3 + \mu_i^4 = M_i \tag{5.84}$$

$$\mu_i^1 - \mu_i^2 + \mu_i^3 - \mu_i^4 = 0 \tag{5.85}$$

$$\mu_i^1 - \mu_i^2 - \mu_i^3 + \mu_i^4 = 0 \tag{5.86}$$
$$\mu_i^1 + \mu_i^2 - \mu_i^3 - \mu_i^4 = -\left(\frac{c+\xi_i}{\delta_i}\right) M_i$$
(5.87)

where (i = x, y, z). Addition of (5.85) and (5.86) yields $\mu_i^1 = \mu_i^2$ and subtraction of (5.86) from (5.85) gives $\mu_i^3 = \mu_i^4$. Similarly, addition of (5.84) and (5.87) yields

$$\mu_i^1 = \mu_i^2 = \frac{M_i}{4} \left[1 - \frac{(c+\xi_i)}{\delta_i} \right]$$
(5.88)

and subtraction of (5.87) from (5.84) gives

$$\mu_i^3 = \mu_i^4 = \frac{M_i}{4} \left[1 + \frac{(c+\xi_i)}{\delta_i} \right]$$
(5.89)

From equations (5.88) and (5.89) it may be seen that the average magnetic moments of the ions are divided into two groups that differ only in their absolute magnitude. Such a type of magnetic ordering is known as *latent antiferromagnetism* (Tolédano & Tolédano, 1987) and differs from ferrimagnetism in that the magnetic moments are associated with one identical type of magnetic ions that are in equivalent crystallographic positions in the paramagnetic phase.

Chapter 6

Discussions

In this chapter physical mechanisms are proposed that can account for the observed structural and magnetic phase transitions in CeSi_x as a function of silicon concentration. The discussions are divided into three parts. First, molecular orbital theory and the phenomenon of π -bonding are introduced and are used to illustrate why the ThSi_2 -type structure of CeSi_2 is expected to be crystallographically unstable in comparison to the AlB₂-type and GdSi₂-type structures formed by the heavy rare-earth 'disilicides' and the GdSi₂-type structure of CeSi_x ($x \leq 1.80$). Second, the ideas presented in the first section are extended and it is suggested how the introduction of silicon vacancies into CeSi_2 effects the electronic band-structure and conduction electron density of CeSi_x . Finally, the magnetic dispersion is calculated for CeSi_x with the tetragonal ThSi_2 -type structure and, using the estimate of the variation of the conduction electron density of CeSi_x as a function of silicon concentration, the subsequent variation of the exchange interaction coefficients and thus the magnetic ordering in CeSi_x , are discussed.

6.1 π -bonding and its effect on the crystallographic instability of CeSi₂

As discussed in § 1.1, the size of the rare-earth ion dictates whether the rare-earth 'disilicide' is formed with the ThSi₂-type, the GdSi₂-type or the AlB₂-type crystal

structure. For the heavy rare-earths whose ionic radii are small, the latter two types of structure are commonly formed. Such structures are 'defect' structures (the 'disilicide' stoichiometry usually being RE_3Si_5), they often exhibit an ordering of the silicon vacancies and they are found to be crystallographically stable. For the lighter rareearth disilicides it is not possible to form the AlB2-type structure as the increased size of the rare-earth ion prevents the formation of the planar silicon sublattice (Mayer et al., 1962). Instead the GdSi₂-type and ThSi₂-type structures are formed. The former is a stable defect structure in which there is the possibility of an ordering of silicon vacancies. However, as shown in § 4.1, there does exist experimental evidence to suggest that rare-earth disilicides with the ThSi₂-type structure are crystallographically unstable. The observations on CeGe₂, CeGa₂ and the pseudo-binaries $CeSi_{2-x}Ge_x$ and $CeSi_{2-x}Ga_x$ indicate that, as well as the size of the rare-earth ion, the electronic configuration and covalent bonding of the non rare-earth atoms also have an important effect in determining the crystal structure formed by the alloy. Indeed, this fact has been previously recognized by Brown (1961) and Mayer et al. (1962) in their respective discussions of the polymorphism of ThSi2 and rare-earth disilicides, in which they concluded that neither factor should be neglected.

The aim of this discussion is to take these factors into consideration and to propose why the AlB₂-type structure of a rare-earth 'disilicide' is energetically more favourable than the GdSi₂-type structure which in turn is more favourable than the ThSi₂-type structure. Thus it will be shown why the ThSi₂-type crystal structure of CeSi₂ is unstable with respect to the GdSi₂-type structure of CeSi_x. Below, following the text of Owen & Brooker (1991), the essential features of molecular orbital theory are introduced. Subsequently it is illustrated how, within molecular orbital theory, the planar silicon sublattice of the AlB₂-type structure is of lower energy than the 'threedimensional graphite' silicon sublattice of the ThSi₂-type. The defect-orthorhombic silicon sublattice of the GdSi₂-type is shown to be intermediary in stability with respect to the latter two, having more electrons involved in π^* -bonding than the hexagonal sublattice but less than the tetragonal sublattice. Finally it is discussed how the results of the diffraction experiments on CeSi_x (1.80 $\leq x \leq 2.00$) are reconciled with the formation of a defect silicon sublattice in the silicon 'poor' phase with the effect of reducing the π^* -bonding.



Figure 6.1: Energy levels of bonding and anti-bonding molecular orbitals.

Introduction to molecular orbital theory

Molecular orbital theory describes the bonding in solids by considering the atomic electron orbitals (AO's) of neighbouring atoms to combine to give delocalized molecular orbitals (MO's) extending over the entire molecule. In the simple molecular orbital theory, a covalent bond involves the overlap of two atomic orbitals on different atoms to give *bonding* and *anti-bonding* molecular orbitals. Electrons in a bonding MO lie in the region of space between the nuclei (though not necessarily on the inter-nuclear axis) and attract the nuclei, holding them together. A bonding MO is thus lower in energy than either of its constituent atomic orbitals. In an anti-bonding MO there is less electron density between the nuclei than for two individual AO's. Consequently the effectiveness of the electronic screening between the two positively charged nuclei is reduced and the electrostatic repulsion between the nuclei is increased. The antibonding MO is thus higher in energy than either of its constituent atomic orbitals, as illustrated in Fig 6.1. Within a solid such molecular orbitals will be broadened into bands.

Fig. 6.2 illustrates the atomic s, p and d orbitals where the shading represents the sign of the electron wavefunction in the orbital lobe. There is a direct correspondence between these pictorial representations and the electron density in an orbital since squaring the wavefunction and integrating over a volume element gives the probability of finding an electron within that volume element. Within molecular orbital theory the combination of the AO's results in three different types of MO that are classified according to their symmetry in a plane perpendicular to the inter-nuclear axis. A ' σ '

MO has the same symmetry as an s AO and may be formed by the overlap of s, p, d and f AO's. A ' π ' MO has the same symmetry as a p AO and may be formed by the overlap of p, d and f orbitals, but not by s orbitals. Similarly a ' δ ' MO has the same symmetry as a d AO and may only be formed by the overlap of d and f orbitals. The first two types of MO are illustrated in Fig. 6.3.

Within molecular orbital theory there are several rules that govern the degree of interaction of the AO's, the construction of the MO's and their subsequent electron filling (Owen & Brooker, 1991). The important rules relevant to the following discussion are summarized below.

- MO's are constructed as a linear combination of AO's. The number of MO's must always equal the initial number of AO's.
- Anti-bonding MO's are slightly more anti-bonding than bonding MO's are bonding as a consequence of a bonding MO bringing the nuclei closer together and thus increasing the inter-nuclear repulsion.
- The degree of interaction of orbitals depends upon how close they are in energy (the strongest interaction is between the orbitals closest in energy) and how diffuse or concentrated the orbitals are. Generally the more diffuse two orbitals are, the less well they overlap.
- For a certain combination of AO's, σ interactions are stronger than π interactions since the σ interaction is due to the head-on overlap of AO's whereas the π interaction results from a side-on overlap.
- The filling of MO's are governed by the same rules as the filling of AO's and hence; electrons fill from the lowest available MO upwards (Aufbau principle), only a maximum of two electrons can occupy any one MO (Pauli's principle), if two or more MO's are degenerate they will be occupied to give the maximum number of parallel electron spins (Hund's first rule).



Figure 6.2: Atomic s, p and d orbitals; shading denotes lobes with a positive sign of the electron wavefunction, clear lobes have a negative sign.



Figure 6.3: The a) σ and b) π molecular orbitals.



Figure 6.4: The planar silicon sublattice in the AlB₂-type structure.

 π -bonding within the silicon sublattice of CeSi_x

A free neutral silicon atom has an electronic configuration $[Ne]2s^22p^2$. For the planar silicon sublattice of the AlB₂-type structure each silicon atom bonds covalently to its three nearest neighbours by the σ -overlap of sp^2 hybrid orbitals. The remaining p electron on each silicon atom resides in a half-filled p orbital lying above and below the bonding plane, as illustrated in Fig. 6.4a, and the silicon sublattice is 'graphitic' in nature (Mayer et al., 1962). There exists the possibility of π -bonding between the p orbitals of neighbouring atoms and for such a structure where the silicon sublattice is planar and all the p AO's on neighbouring atoms are parallel, this is consistent with each AO being exactly half-filled and their overlap resulting in a full bonding MO (for an extended array of atoms in a solid this is referred to as the π -band) and an empty anti-bonding MO (π^* -band). It is to be noted that, though each silicon atom has only one p electron with which to form a π -bond with one of its three neighbouring atoms, by analogy to the well known π -bonding in benzene and graphite (Borg & Dienes, 1992a), the p electron may be considered to be delocalized in space such that there is an extended positive and negative 'lobe' of the wavefunction above and below the bonding plane, as illustrated in Fig. 6.4b.

Now taking into consideration the overlap of the conduction electron wavefunctions of the rare-earth ions and those of the p orbitals of the planar silicon sublattice, the conduction electrons may only occupy the previously empty π^* -band. Such an occupation of the anti-bonding MO's will reduce the stability of the structure compared to that where the π^* -band is empty. In a hypothetical situation where both silicon atoms A and B gain an electron from the conduction band such that the atomic p



Figure 6.5: Expected orientation of two atomic p orbitals on neighbouring silicon atoms A and B when a) both contain one electron, b) both contain two electrons.

orbital on each atom is filled, then Fig. 6.5 illustrates the relative orientation expected for the two AO's as a result of their Coulomb interaction; such an orientation will minimize the overlap of the electron wavefunctions and thus minimize the energy associated with them. In molecular orbital theory this would correspond to the two atoms having both a full bonding MO and a full anti-bonding MO and the energy of the configuration would be minimized by the minimal overlap of the neighbouring atomic p orbitals.

As previously discussed in § 1.1, the silicon sublattice of CeSi₂ resembles a threedimensional graphite structure. The sublattice is illustrated in Fig. 6.6a along with the expected orientation of the atomic p orbitals (neglecting for now the presence of the cerium sublattice). It can be seen that the buckled layers of silicon-silicon chains are joined by bonds parallel to the *c*-axis and the orientation of the chains rotates by 90° for subsequent layers such that the chains run successively along the a or baxes. This results in there being four p orbitals per crystallographic unit cell that are orientated parallel to the p orbital on a neighbouring silicon atom, and four that are

Taking into consideration only the π -bonding within CeSi₂, a simple but consistent representation of the energy level scheme and band filling may be obtained via the rules of molecular orbital theory. First of all, rather than making an attempt to consider the overlap of atomic orbitals of all of the silicon atoms within the silicon sublattice of CeSi₂, the problem may be simplified by defining a smaller 'molecularunit', the repetition of which will reproduce the complete silicon sublattice. This approach is similar to that of *Hückel theory* (Albright *et al.*, 1985) in which the



Figure 6.6: a) The silicon sublattice of tetragonal CeSi₂ illustrating the directions of the π -bonding p orbitals on each atom. b) The six configurations of the π -bonding p orbitals in a 'molecular-unit', their relative energies and the proposed number of electrons involved in π -bonding within each molecular-unit.



Figure 6.7: Hypothetical energy level diagram for π -bonding in CeSi₂.

orbital energies and electron wavefunctions of carbon molecules containing extended π -bonding chains are calculated, in a first approximation, by taking into consideration an *allyl* group, i.e. a chain of three carbon atoms. An appropriate molecular-unit for our purpose consists of a chain of three silicon atoms and their associated σ -, π - and dangling-bonds. For such a molecular-unit there are only six possible configurations of the π -bonding atomic p orbitals on each of the three silicon atoms. These are illustrated in Fig. 6.6b along with their relative energies and the number of electrons proposed to be involved in π -bonding within the molecular-unit in view of the relative orientation of the atomic orbitals. Such a representation of the relative energies of the orbital configurations is consistent with that expected for allyl within Hückel theory. It can be seen from Fig. 6.6a that the silicon sublattice is composed of configurations (1) \rightarrow (5). The highest energy configuration, for which each silicon atom in the molecular-unit has a full atomic p orbital and their π -overlap is minimized by their mutual orthogonal orientation, does not occur.

The combination of three AO's of the molecular-unit necessarily results in three MO's that are broadened into bands within the solid. Following the notation of Borg & Dienes (1992b), the π^* -band will correspond to the least favourable overlap of the three AO's of the molecular-unit and will be *anti-bonding* in nature, the π band will correspond to the most favourable overlap and will be bonding in nature, and the remaining band corresponding to the intermediary overlap configurations will be a non-bonding band. Within the silicon sublattice of CeSi₂ there are thirty possible chains of three silicon atoms that may be chosen as the molecular-unit. Taking into consideration all of these chains and summing up the number of electrons involved in π -bonding within each (using the proposed numbers shown in Fig. 6.6b for the different orientations of the p orbitals on each silicon atom in the chain) then on average, a molecular-unit in the CeSi₂ lattice has 4.267 electrons involved in π bonding. Since each MO may hold a maximum of two electrons, this results in a partial filling of the π^* -band for CeSi₂. Accordingly the energy level scheme and band filling for the π -bonding molecular orbitals of CeSi₂ are illustrated in Fig. 6.7. Though this discussion is simple and approximate, the partial filling of the π^* -band is consistent with the absence of the highest energy molecular-unit (configuration (6)) in the silicon sublattice.

Reduction in π^* -bonding following an introduction of vacancies and a distortion of the silicon sublattice of CeSi₂

For 'ideal' sp^2 bonding within an all- sp^2 bonded tetragonal network, all silicon-silicon bond lengths should be equivalent and thus all bond angles 120° (Corkhill *et al.*, 1992). Such conditions are not quite satisfied for the tetragonal silicon sublattice of CeSi₂ where bond angles are approximately 121° and 119°. A summary of the lattice parameters, silicon-silicon bond lengths and bond angles is given in Table 6.1 for the CeSi_x phases examined by neutron powder diffraction (§ 3.3 and § 4.1). The data at 1.5K has been used since the resolution of two-phase samples was the most accurate at this temperature due to the large variation in the lattice parameters of the two phases. The significant fact to be observed from Table 6.1 is that the stable single phase of CeSi_{1.80} (F) and the orthorhombic silicon 'poor' phases of CeSi_x (x = 1.85, 2.16) have bond lengths and bond angles that are less equivalent and further removed from 120° than those of the tetragonal phases. Thus it may be concluded that the energetic stability of a tetragonal all- sp^2 bonded network is not the driving factor responsible for the phase separation in CeSi_x ($1.80 \leq x \leq 2.00$) samples but rather the ordering of silicon vacancies.

Examination of the lattice parameters in Table 6.1 shows that the stable crystal lattice of CeSi_x is one in which there is an introduction of silicon vacancies, a contraction of the *c*-axis and an orthorhombic distortion and expansion of the *a* and *b* axes. In order to try to understand why such a defect-distorted sublattice is more stable than the silicon sublattice of CeSi_2 , a hypothetical situation will be considered where one silicon atom is removed from the crystallographic unit cell and a tetragonal \rightarrow orthorhombic distortion is allowed to occur that is consistent with the one observed experimentally. As there are four formula units of CeSi_2 in the unit cell, this discussion is thus considering a phase with the stoichiometry $\operatorname{CeSi}_{1.75}$. Fig. 6.8a illustrates a plausible movement of silicon atoms when an atom A is removed from the tetragonal silicon sublattice of CeSi_2 . Fig. 6.8b then represents the hypothetical bonding of the defect-distorted sublattice of $\operatorname{CeSi}_{1.75}$. Such a re-arrangement of atoms, as suggested by the experimental observations, will reduce the number of perpendicularly aligned neighbouring *p* AO's from four per unit cell to three. Thus the defect-orthorhombic

	CeSi _{1.80} (F)	CeSi _{1.85}		CeSi _{2.16}	
phase		Si 'poor'	Si 'rich'	Si 'poor'	Si 'rich'
a (Å)	4.1625(2)	4.1618(3)	4.1537(1)	4.1615(4)	4.1522(1)
b (Å)	4.1549(2)	4.1561(3)		4.1537(3)	
c (Å)	13.8369(4)	13.8386(4)	14.0356(7)	13.8348(6)	14.0411(4)
Si-Si _a (Å)	2.328(4)	2.329(4)	2.370(2)	2.341(6)	2.380(4)
Si-Si _b (Å)	2.408(3)	2.414(4)		2.395(9)	
Si-Si _c (Å)	2.329(7)	2.322(9)	2.366(4)	2.326(16)	2.348(8)
(Si^Si)a	126.8(3)°	126.6(4)°	122.4(2)°	125.4(5)°	121.5(3)°
(Si^Si)₅	119.3(2)°	118.8(3)°		120.3(6)°	
(Si^Si)ac	116.6(2)°	116.7(2)°	118.8(1)°	117.3(3)°	119.3(2)°
(Si^Si) _{bc}	120.4(1)°	120.6(2)°		119.9(4)°	

Table 6.1: Lattice parameters, bond lengths and bond angles from neutron powder diffraction refinements of $CeSi_x$ samples at 1.5K.

sublattice is necessarily more stable than the tetragonal sublattice due to a reduction in the number of electrons in the anti-bonding π^* -band. For CeSi_x the possibility of forming the AlB₂-type structure with the most stable planar arrangement of silicon atoms is restricted by the size of the Ce³⁺ ion.

The above discussion remains qualitative but it is consistent both with the observations on CeSi_x and the other rare-earth 'disilicides'. For the latter, the reduction in the size of the rare-earth atom with increasing atomic number will decrease the possibility of overlap of the 4f, 5d and 6s wavefunctions with those of the silicon 3p electrons, thus reducing the possibility of filling the anti-bonding MO's of the silicon atoms and hence favouring the formation of the planar silicon sublattice. As discussed in § 1.1, such a sublattice is consistently formed as a stable single phase for the heavy rare-earth 'disilicides'.

The arguments above are also consistent with the observations on the pseudobinary 'disilicides' $\text{CeSi}_{2-x}\text{Ge}_x$ and $\text{CeSi}_{2-x}\text{Ga}_x$ in § 4.1. Recalling that gallium and germanium have the electronic configurations $[\text{Ar}]3d^{10}4s^24p^1$ and $[\text{Ar}]3d^{10}4s^24p^2$ remotion of silicon atoms
 distortion of lattice



Figure 6.8: Hypothetical arrangement of silicon atoms in the defect, orthorhombically distorted silicon sublattice of CeSi_{1.75}.

spectively, then germanium with an identical outer electron configuration as silicon would be expected to exhibit the same type of crystal chemistry, within the restrictions of its increased size. The interchange of silicon and germanium atoms within the silicon sublattice of CeSi₂ would still retain the same number of $sp^2 \sigma$ -bonds and π -bonds between these atoms. For the substitution of gallium however, the three sp^2 electrons on each Ga atom will overlap and form σ -bonds with the three neighbouring atoms, leaving no electrons in its 4p orbital. Consequently there is no possibility of forming π^* -bonds with any neighbouring silicon atoms that have two electrons in the 3p orbital, and thus the energy of π^* -bonding within the lattice will be reduced. The observation of the coexistence of two isostructural phases in CeSi_{2-x}Ga_x ($0.2 \le x \le 0.5$) similar to that within the Ce-Si system may readily be understood by an ordering of the available gallium atoms within one of the two phases, such that the π^* -bonding within this phase is minimized. The same reduction in the number of π^* -bonds is thus obtained but in this case by the presence of gallium atoms rather than the absence of silicon atoms.

The enhancement observed in § 4.4 for $\gamma(x)$, the linear coefficient of the specificheat capacity of CeSi_x, as a function of x may also be understood within the ideas



Figure 6.9: Energy level diagram for π -bonding in a) CeSi_{1.75} and b) CeSi_x (where 1.75 < x < 2.0).

presented above. Continuing to take the case of $\text{CeSi}_{1.75}$ as an example of a silicon deficient stoichiometry and repeating the same calculation as performed above for CeSi_2 regarding the number of electrons within the atomic p orbitals of the average molecular-unit, then for the defect lattice of Fig. 6.8b there are 28 combinations of three silicon lattice sites that may compose a molecular-unit. Two of the silicon lattice sites will now contribute no p electrons to the molecular orbitals as all of their $3s^23p^2$ electrons are involved in σ -bonding within the sublattice. Taking this factor into consideration and using, once again, the number of electrons proposed to be involved in π -bonding within a molecular-unit as illustrated in Fig. 6.6b, then averaging the total number of electrons involved in π -bonding over the 28 possible choices of the molecular-unit for $\text{CeSi}_{1.75}$, gives an average of 3.786 electrons. Fig. 6.9a illustrates the corresponding band filling of the π -bonding MO's for $\text{CeSi}_{1.75}$ with a partial filling of the non-bonding band (n.b.b.) and an empty π^* -band.

It should be stressed that the stoichiometry $\text{CeSi}_{1.75}$ has just been taken as one example of a silicon deficient sample and it does not necessarily represent the most stable silicon concentration for CeSi_x in the GdSi_2 -type structure. The choice of x =1.75 has only been encouraged by the absence of observations of two-phase samples for this starting stoichiometry and its convenience when performing the electron counting exercises above. By comparison of Figures 6.7 and 6.9a, it may be argued that at some intermediate silicon concentration x (where 1.75 < x < 2.0) there will be a crossover of the Fermi level from the π^* -band to the non-bonding band (n.b.b.) with increasing x, as illustrated in Fig. 6.9b. It is thus reasonable to interpret the resulting increase in the density of states $g(\varepsilon_F)$ as arising from the bottom of the π^* -band. As the band edge is approached the effective mass of the electron becomes large as $m^* \propto 1/\frac{\partial^2 \epsilon(k)}{\partial k^2}$, yielding the experimentally observed enhancement of $\gamma(x)$ as a function of x. This idea will be discussed in more detail in the next section. For the moment, the important observation to be noted from this discussion is how the presence of vacancies in the silicon sublattice of CeSi₂ will cause a decrease in the number of electrons in the anti-bonding π^* -band and thus an increased stability of the CeSi_x lattice compared to that of CeSi₂.

6.2 Effect of a reduction of π^* -bonding on the electronic band-structure and conduction electron density of CeSi_x

In discussing the π -bonding in CeSi_x within molecular orbital theory we have greatly simplified the problem by dealing with the overlap of atomic orbitals of a discrete number of silicon atoms. The preceeding discussion has not taken into consideration all of the silicon atoms that comprise one crystallographic unit cell. Instead, the problem has been simplified one stage further by discussing the overlap of the atomic orbitals of just three silicon atoms that comprise a 'molecular-unit', the repetition of which may describe the silicon sublattice of CeSi₂. In order to consider the effect of π -bonding on a macroscopic level it is more appropriate to discuss the electronic band-structure and density of states of CeSi_x, whereby the Fourier transformation process enables one to take into account all of the unit cells within the crystal. However, in view of the absence of quantitative electronic band-structure calculations, the following discussion remains both qualitative and speculative.

This discussion makes the assumption that a 'tight-binding approximation' (Ashcroft & Mermin, 1981) may be used to describe the electronic band-structure of CeSi_x . Such an approximation is appropriate when the overlap of atomic wave functions of neighbouring atoms is sufficient to cause the idea of isolated atoms to be incorrect, but

not so much such that the atomic description is completely irrelevant. The crystal Hamiltonian is considered to be represented by

$$\mathcal{H} = \mathcal{H}_{at} + \Delta U(\mathbf{r}) \tag{6.1}$$

where \mathcal{H}_{at} is the Hamiltonian of a single atom located at a lattice point and $\Delta U(\mathbf{r})$ is a function containing all of the corrections to the atomic potential \mathcal{H}_{at} required to produce the full periodic potential of the crystal. It is assumed that the bound levels of the atomic Hamiltonian are well localized, i.e., if ψ_n is a bound level of \mathcal{H}_{at} for an atom at the crystal origin,

$$\hat{\mathcal{H}}\psi_n = \epsilon_n \psi_n \tag{6.2}$$

and thus $\psi_n(r)$ is required to be very small when r exceeds a distance of the order of the lattice constant. Within the tight-binding approximation the atomic wavefunction $\psi_n(r)$ of the n^{th} atomic energy level may be expressed by

$$\psi_n(r) = \sum_{R} e^{ik.R} \phi_n(r-R)$$
(6.3)

where R is a lattice site vector and the functions ϕ_n are known as Wannier functions and form a complete orthogonal set for all n and R. A general feature of the tightbinding approximation is the following relationship between the bandwidth (i.e. the spread between the maximum and minimum energies in the band) and the overlap integral γ_{ij} ,

$$\gamma_{ij}(R) = -\int dr \phi_i^*(r) \Delta U(r) \phi_j(r-R)$$
(6.4)

For any arbitrarty direction within the crystal, then from (6.4) when the γ_{ij} are small the bandwidth is correspondingly small, and vice versa. Similarly, if the radius of the atomic species increases (for the same direction within the crystal and interatomic separations), the increase in the wavefunction overlap will cause an increase in the bandwidth.

The density of electronic energy levels (henceforth referred to as the density of states, DOS) in a solid is given by

$$g(\varepsilon) = \sum_{n} g_n(\varepsilon) \tag{6.5}$$

where $g_n(\varepsilon)$ is the density of levels in the n^{th} band and may be determined from

$$g_n(\varepsilon) = \int_{S_n(\varepsilon)} \frac{dS}{4\pi^3} \frac{1}{|\nabla \varepsilon_n(k)|}$$
(6.6)



Figure 6.10: Schematic representation of the electronic band-structure of $CeSi_2$ for an arbitrary direction within the first Brillouin zone. The position of the Fermi level is given by the dashed line and the boundary of the Brillouin zone is marked by the dot-dash line.

 $S_n(\varepsilon)$ is the surface in reciprocal space of constant energy ε and $\nabla \varepsilon_n(k)$ is the gradient in k-space of $\varepsilon_n(k)$. Equation (6.6) thus gives a direct relationship between the DOS and the electronic band-structure.

In analogy to the discussion of § 6.1, it is proposed that the electronic bandstructure of CeSi₂ may be represented schematically by Fig. 6.10 for an arbitrary direction within the first Brillouin zone. Within this idealization, the finite overlap of the 3s and 3p orbitals of neighbouring silicon atoms is represented by the relatively broad sp^2 and π -bands (both bonding and anti-bonding). It is assumed that the cerium ions are trivalent (a supposition that is supported by valence-band photoemission experiments on CeSi₂, Lawrence *et al.*, (1982), which indicate trivalency of the cerium ions as opposed to fractional valence) and that the overlap of the cerium 5d and 6s wavefunctions constitutes the broad conduction band whose band-structure has been approximated by that of a free electron gas. The following discussion of the electronic band-structure and position of the Fermi level for CeSi₂ and CeSi_x makes the assumption that the cerium 4f energy level remains well localized around the cerium ion and is unaffected by the changes in the band filling as a function of silicon concentration, x. Thus, for these purposes, the cerium 4f band and all lower energy bands have been neglected in Fig. 6.10.



Figure 6.11: Schematic representation of the electronic band-structure and the Fermi energy for CeSi₂, CeSi_{1.83} and CeSi_x (x < 1.83). The dashed line indicates the position of the Fermi level and the shading represents the band filling. The dot-dash line marks the boundary of the first Brillouin zone.

As discussed in § 6.1, the physical overlap of the silicon p orbitals within the silicon sublattice of CeSi₂ plausibly suggests a partial filling of the anti-bonding π^* -band. Similarly, the reduction of π -bonding in CeSi_x due to the introduction of silicon vacancies suggests an emptying of the π^* -band as a function of x, as was illustrated in Fig. 6.9. Within a rigid-band model the effect of silicon vacancies on the electronic band-structure of CeSi₂ will not significantly effect the overall shape of the bands but only cause a shift in the energy of the bands such that the position of the Fermi level moves to lower energies. In this simple approximation the electronic band-structure of CeSi_x will be considered to be identical to that of CeSi₂. Fig. 6.11 illustrates the

position of the Fermi level expected for CeSi₂, CeSi_{1.83} and CeSi_x (x < 1.83). Once again, the position of ε_F for CeSi_{1.83} has been fixed such that $\nabla \varepsilon_{\pi^*}(k) \approx 0$ and thus from equation (6.6) there is a corresponding enhancement of $g_n(\varepsilon_F)$, reflecting the experimentally observed enhancement in the linear specific-heat coefficient $\gamma(x)$ as a function of x (§ 4.4). From Fig. 6.11 it is suggested that the effect of the introduction of silicon vacancies into the crystal lattice of CeSi₂ and the subsequent reduction in π^* -bonding is to cause a shift of the Fermi level to lower energies and a decrease in the conduction electron density of CeSi_x with decreasing x.

6.3 The non-magnetic \rightarrow magnetic phase transition in CeSi_x

Having gained an understanding of how the introduction of silicon vacancies into the CeSi₂ lattice will affect the conduction electron density in $CeSi_x$, the aim of this discussion is to use this insight to determine the effect of silicon vacancies on the ground state magnetic order of $CeSi_x$. Since the dominant exchange interaction between cerium ions is an indirect exchange via a polarization of the conduction electrons (§ 2.3), a variation in the conduction electron density will have a significant effect on the magnetic interactions between cerium ions in CeSi_x . To accomplish this aim, first the magnetic dispersion in CeSi_x will be calculated for nearest neighbour and next-nearest neighbour exchange between cerium atoms located on a tetragonal CeSi_{x} lattice. Then the magnetic ordering predicted by such a calculation will be discussed as a general function of the exchange interaction parameters. Finally, using the discussion of § 6.2 as an estimate for the variation of the conduction electron density in $CeSi_x$ with x, the corresponding variation in the exchange parameters will be determined from RKKY theory and a tentative explanation proposed for the nonmagnetic \rightarrow magnetic phase transition in CeSi_x with decreasing x. Once again, it is stressed that throughout this discussion the cerium 4f electrons are considered to remain well localized around the cerium ions, independent of the presence or absence of silicon vacancies in the lattice.

Starting Hamiltonian

The Heisenberg exchange Hamiltonian for CeSi_x in zero external magnetic field is

$$\mathcal{H} = -\frac{1}{2} \sum_{l,l'} \mathcal{J}_{ll'} \left(R_l - R_{l'} \right) S_{l} S_{l'}$$
(6.7)

where $\mathcal{J}_{ll'}$ is the exchange parameter between two spins S_l and $S_{l'}$ on lattice sites land l' at positions R_l and $R_{l'}$ respectively. Following the mean-field theory approach used by Reimers *et al.* (1991) to discuss the magnetic ordering in pyrochlores, here the same approach will be used to diagonalize the exchange Hamiltonian (6.7) by a Fourier transformation and subsequently determine the dispersion of the correspond-



Figure 6.12: a) The two Bravais sublattices composing the cerium sublattice of $CeSi_x$, b) the labelling scheme used.

ing eigenvalues $\lambda_i(q)$ (i = 1, ...). Such a calculation will enable the magnetic order of the ground state of CeSi_x to be predicted since this is determined by the maximum $\lambda_i(q)$, by which the energy of the system is minimized.

The crystal lattice of CeSi_x (described by the tetragonal space group $I4_1/amd$) is not a Bravais lattice and thus the Hamiltonian (6.7) may not be diagonalized by a simple Fourier transformation. To overcome this problem, the CeSi_x lattice is considered to be composed of two body-centered tetragonal Bravais sublattices as shown in Fig. 6.12a. Though each sublattice does contain two cerium atoms, because the body centering translation $(t=\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is a lattice translation, the point group symmetry and orientation of the two cerium lattice sites are identical and the sublattice is Bravais. In the following discussion the subscripts l, l' will be used to denote two sites in the sublattice α , and m, m' will denote sites on the sublattice β . The Fourier transforms of the exchange interaction parameters for inter-sublattice exchange are to be defined by

$$\mathcal{J}_{ll'}^{\alpha}(R_l-R_{l'})=\frac{1}{N}\sum_{q}\mathcal{J}^{\prime\alpha}(q)\,e^{iq.(R_l-R_{l'})}$$

and

$$\mathcal{J}^{\beta}_{mm'}(R_m - R_{m'}) = \frac{1}{N} \sum_{q} \mathcal{J}^{\prime\beta}(q) e^{iq.(R_m - R_{m'})}$$
(6.8)

and for the intra-sublattice exchange,

$$\mathcal{J}_{lm}^{\alpha\beta}\left(R_{l}-R_{m}\right)=\frac{1}{N}\sum_{q}\mathcal{J}\left(q\right)e^{iq\left(R_{l}-R_{m}\right)}$$
(6.9)

where N is the total number of unit cells in the crystal. When $(R_l - R_{l'}) = (R_m - R_{m'})$ then because the two sublattices are equivalent, $\mathcal{J}^{\prime \alpha}(q) = \mathcal{J}^{\prime \beta}(q)$. For the following discussion the superscripts α and β will be dropped and the Fourier transform of the inter-sublattice exchange parameter will by given by $\mathcal{J}'(q)$. The Fourier transforms of the spins are defined by

$$S_l = \frac{1}{\sqrt{N}} \sum_{q} S_{q} e^{iq.R_l}$$

 and

$$S_{l'} = \frac{1}{\sqrt{N}} \sum_{q'} S_{q'} e^{iq'.R_{l'}}$$
(6.10)

Substituting (6.8), (6.9) and (6.10) into (6.7) and using the standard result

$$\frac{1}{N} \sum_{l} e^{i(q-q') \cdot R_{l}} = \delta(q-q') = \begin{cases} 0 & q \neq q' \\ 1 & q = q' \end{cases}$$
(6.11)

where q and q' are wavevectors in the first Brillouin zone, the Fourier transformed Hamiltonian of CeSi_x is given by

$$\mathcal{H} = -\frac{1}{2} \sum_{q} \mathcal{J}'(q) S_{q} S_{-q} - \frac{1}{2} \sum_{q} \mathcal{J}(q) S_{q} S_{-q}$$
(6.12)

It should be noted that for inter-sublattice exchange

$$\mathcal{J}'(q) = \mathcal{J}'(-q) \tag{6.13}$$

whereas for intra-sublattice exchange

$$\mathcal{J}(q) = \mathcal{J}^*(-q) \tag{6.14}$$

since the vector joining sites on different sublattices is not a lattice vector.

Atom label	Position in the unit cell	Nearest neighbour atoms
ν, μ	$R_l^{ u}$	R^{μ}_{m}
α1	(0,0,0)	$2 \times \beta_1, 2 \times \beta_2$
β_1	$\left(0,\frac{1}{2},\frac{1}{4}\right)$	$2 \times \alpha_1, 2 \times \alpha_2$
α_2	$\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$	$2 \times \beta_1, 2 \times \beta_2$
β_2	$\left(\frac{1}{2},0,-\frac{1}{4}\right)$	$2 \times \alpha_1, 2 \times \alpha_2$

Table 6.2: Nearest neighbours to each of the four cerium sites of $CeSi_x$ shown in Fig. 6.12.

Calculation for nearest neighbour interactions

The four cerium atoms in the unit cell of CeSi_x have been labelled α_1 , β_1 , α_2 and β_2 as shown in Fig. 6.12b. Taking into consideration only the nearest neighbour interactions for a tetragonal CeSi_x lattice then Table (6.2) lists the nearest neighbour cerium ions to each of the four cerium ion sites. It can be seen that the nearest neighbour approximation involves the exchange interactions between cerium ions on different sublattices only.

The magnetic dispersion will be calculated along several symmetry directions within the first Brillouin zone, illustrated for the tetragonal CeSi_x lattice in Fig. 6.13 where the reciprocal lattice basis vectors are denoted by g_1 , g_2 and g_3 . Within the notation used here the unit cell lattice vectors are denoted by a, b, and c and the reciprocal lattice basis vectors τ_i (i = x, y, z) are defined by

$$\tau_{x} = \frac{2\pi}{a.(b \times c)} b \times c, \quad \tau_{y} = \frac{2\pi}{a.(b \times c)} c \times a, \quad \tau_{z} = \frac{2\pi}{a.(b \times c)} a \times b \quad (6.15)$$

An arbitrary reciprocal lattice vector q is defined by

$$q = q_x \tau_x + q_y \tau_y + q_z \tau_z \tag{6.16}$$

where q_x , q_y and q_z are scalars. Thus for the tetragonal CeSi_x lattice,

$$q.(R_l - R_m) = \frac{2\pi}{a} (R_{l_x} - R_{m_x}) q_x + \frac{2\pi}{a} (R_{l_y} - R_{m_y}) q_y + \frac{2\pi}{c} (R_{l_x} - R_{m_x}) q_z \quad (6.17)$$

From (6.9) the Fourier transform of the intra-sublattice exchange parameter is defined by

$$\mathcal{J}(q) = \frac{1}{N} \sum_{l,m} \mathcal{J}_{lm}^{\alpha\beta} \left(R_l - R_m \right) e^{-iq. \left(R_l - R_m \right)}$$
(6.18)



Figure 6.13: The Brillouin some for a tetragonal body-centered Bravais lattice with c > a, courtesy of Bradley & Cracknell (1972). g_1 , g_2 and g_3 are the basis vectors of the reciprocal lattice and the coordinates of the translations of g_1 , g_2 and g_3 with respect to the k_m , k_y and k_a axes are $\frac{2\pi}{ca}(0, c, a)$, $\frac{2\pi}{ca}(c, 0, a)$ and $\frac{2\pi}{ca}(1, 1, 0)$, respectively. With respect to the basis vectors g_1 , g_2 and g_3 , the coordinates of the points in the Brillouin some are $\Gamma = (000)$, $N = (0\frac{1}{2}0)$, $X = (00\frac{1}{2})$, $Z = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ and $P = (\frac{1}{4}\frac{1}{4}\frac{1}{4})$.

Performing the sum over all N unit cells in the crystal for each of the four cerium lattice sites l in a unit cell over the four nearest neighbours m listed in Table 6.2, then for nearest neighbour exchange

$$\mathcal{H} = -\frac{1}{2} \sum_{\boldsymbol{q}} \mathcal{J}(\boldsymbol{q}) \boldsymbol{S}_{\boldsymbol{q}} \boldsymbol{S}_{-\boldsymbol{q}}$$
(6.19)

where the exchange interaction matrix $\mathcal{J}(q)$ is given by

$$\mathcal{J}(q) = \begin{pmatrix} 0 & \mathcal{J}_{\alpha_{1}\beta_{1}}(q) & 0 & \mathcal{J}_{\alpha_{1}\beta_{2}}(q) \\ \mathcal{J}_{\beta_{1}\alpha_{1}}(q) & 0 & \mathcal{J}_{\beta_{1}\alpha_{2}}(q) & 0 \\ 0 & \mathcal{J}_{\alpha_{2}\beta_{1}}(q) & 0 & \mathcal{J}_{\alpha_{2}\beta_{2}}(q) \\ \mathcal{J}_{\beta_{2}\alpha_{1}}(q) & 0 & \mathcal{J}_{\beta_{2}\alpha_{2}}(q) & 0 \end{pmatrix}$$
(6.20)

Putting $\mathcal{J}_{lm}^{\alpha\beta}(R_l-R_m)\equiv \mathcal{J}_1$ since all the cerium-cerium distances are equivalent, the matrix elements are explicitly

$$\mathcal{J}_{\alpha_{1}\beta_{1}}\left(q\right) = \mathcal{J}_{\alpha_{2}\beta_{2}}\left(q\right) = 2\mathcal{J}_{1}\left[\cos\pi q_{y}\cos\frac{\pi}{2}q_{z} - i\cos\pi q_{y}\sin\frac{\pi}{2}q_{z}\right]$$
$$\mathcal{J}_{\beta_{1}\alpha_{2}}\left(q\right) = \mathcal{J}_{\alpha_{1}\beta_{2}}^{*}\left(q\right) = 2\mathcal{J}_{1}\left[\cos\pi q_{x}\cos\frac{\pi}{2}q_{z} - i\cos\pi q_{x}\sin\frac{\pi}{2}q_{z}\right]$$
(6.21)

and

$$\mathcal{J}_{oldsymbol{eta}_{1}lpha_{1}}\left(q
ight)=\mathcal{J}^{*}_{lpha_{1}oldsymbol{eta}_{1}}\left(q
ight)$$

$$\mathcal{J}_{\alpha_{2}\beta_{1}}(q) = \mathcal{J}^{*}_{\beta_{1}\alpha_{2}}(q)$$

$$\mathcal{J}_{\beta_{2}\alpha_{1}}(q) = \mathcal{J}^{*}_{\alpha_{1}\beta_{2}}(q)$$

$$\mathcal{J}_{\beta_{2}\alpha_{2}}(q) = \mathcal{J}^{*}_{\alpha_{2}\beta_{2}}(q)$$

(6.22)

The crystallographic unit cell of CeSi_x contains four cerium atoms and thus there are four eigenvalues $\lambda_i(q)$ (i = 1, 2, 3, 4) of the diagonalized exchange interaction matrix (6.20). These are determined by

$$\det \left(\lambda I - \mathcal{J}(q)\right) = 0 \tag{6.23}$$

where I is the unit matrix, i.e.

$$\begin{array}{c|cccc} \lambda & \mathcal{J}_{\alpha_{1}\beta_{1}}\left(q\right) & 0 & \mathcal{J}_{\alpha_{1}\beta_{2}}\left(q\right) \\ \mathcal{J}_{\beta_{1}\alpha_{1}}\left(q\right) & \lambda & \mathcal{J}_{\beta_{1}\alpha_{2}}\left(q\right) & 0 \\ 0 & \mathcal{J}_{\alpha_{2}\beta_{1}}\left(q\right) & \lambda & \mathcal{J}_{\alpha_{2}\beta_{2}}\left(q\right) \\ \mathcal{J}_{\beta_{2}\alpha_{1}}\left(q\right) & 0 & \mathcal{J}_{\beta_{2}\alpha_{2}}\left(q\right) & \lambda \end{array} \right| = 0$$
 (6.24)

and may be shown to be

$$\lambda_{1,2}(q) = \pm 2\mathcal{J}_1 \left[\cos^2 \pi q_x + \cos^2 \pi q_y + 2\cos \pi q_x \cos \pi q_y \left(1 - 2\cos^2 \frac{\pi}{2} q_z \right) \right]^{\frac{1}{2}}$$

$$\lambda_{3,4}(q) = \pm 2\mathcal{J}_1 \left[\cos^2 \pi q_x + \cos^2 \pi q_y - 2\cos \pi q_x \cos \pi q_y \left(1 - 2\cos^2 \frac{\pi}{2} q_z \right) \right]^{\frac{1}{2}}$$
(6.25)

Within a mean-field approximation, the magnetic ordering temperature can be shown to be proportional to the algebraic sum of the exchange interactions on a given atom. This constraint may be expressed (Smart, 1966) by

$$k_B \theta_c = \frac{2}{3} S(S+1) \sum_{m=1}^{N'} z_m \mathcal{J}_m$$
(6.26)

where θ_c is the Curie temperature, S is the spin on the atom in units of \hbar , z_m is the number of m^{th} nearest neighbours of a given atom, \mathcal{J}_m is the exchange interaction between m^{th} neighbours and N' is the number of sets of neighbours for which $\mathcal{J}_m \neq 0$. For CeSi_x where $\theta_c \approx 12$ K and the total spin on each Ce³⁺ ion is $J = \frac{5}{2}$,

$$\sum_{m=1}^{N'} z_m \mathcal{J}_m = 0.177 \quad \text{meV}$$
(6.27)

Thus for the nearest neighbour approximation, the exchange interaction parameter \mathcal{J}_1 is constrained to be equal to 0.044 meV. Figures 6.14 to 6.17 illustrate the dispersion



Figure 6.14: The eigenvalues $\lambda_i(q)$ (i = 1, ..., 4) along ΓN .



Figure 6.15: The eigenvalues $\lambda_i(q)$ (i = 1, ..., 4) along XZ (following a direct path in reciprocal space from the point X to the point Z, and with the wavevector q measured from the point X).



Figure 6.16: The eigenvalues $\lambda_i(q)$ (i = 1, ..., 4) along ΓX .



Figure 6.17: The eigenvalues $\lambda_i(q)$ (i = 1, ..., 4) along ΓZ .

of $\lambda_i(q)$ (i = 1...4) calculated from (6.25) along the ΓN , XZ, ΓX and ΓZ directions in the Brillouin zone (illustrated in Fig. 6.13).

Figures 6.14 to 6.17 illustrate that within the first Brillouin zone the maxima in $\lambda(q)$ always occur for q = 0. Thus, within the nearest neighbour approximation, the magnetic propagation vector (as defined in equation (2.45)) that describes the magnetic ordering of the ground state of CeSi_x is $q_m = 0$. The possible types of order that are consistent with $q_m = 0$ are either ferromagnetic ordering of the cerium magnetic moments or ferromagnetic order (due to the exchange force interactions) coupled with the existence of an induced antiferromagnetic order (due to relativistic interactions). The antiferromagnetic component would be much weaker that the ferromagnetic component and cause a weak modulation of the ferromagnetically ordered moments, as described in § 5.2.

Calculation for nearest and next-nearest neighbour interactions

The next-nearest neighbour exchange interaction for CeSi_x involves the exchange between cerium ions on one sublattice and is represented in Fig. 6.12b by \mathcal{J}'_2 . The next-nearest neighbour atoms are the corner atoms in the basal plane of a sublattice. For the nearest and next-nearest neighbour approximation then (6.20) becomes

$$\mathcal{J}(q) = \begin{pmatrix} \mathcal{J}_{\alpha_{1}\alpha_{1}}(q) & \mathcal{J}_{\alpha_{1}\beta_{1}}(q) & 0 & \mathcal{J}_{\alpha_{1}\beta_{2}}(q) \\ \mathcal{J}_{\beta_{1}\alpha_{1}}(q) & \mathcal{J}_{\beta_{1}\beta_{1}}(q) & \mathcal{J}_{\beta_{1}\alpha_{2}}(q) & 0 \\ 0 & \mathcal{J}_{\alpha_{2}\beta_{1}}(q) & \mathcal{J}_{\alpha_{2}\alpha_{2}}(q) & \mathcal{J}_{\alpha_{2}\beta_{2}}(q) \\ \mathcal{J}_{\beta_{2}\alpha_{1}}(q) & 0 & \mathcal{J}_{\beta_{2}\alpha_{2}}(q) & \mathcal{J}_{\beta_{2}\beta_{2}}(q) \end{pmatrix}$$
(6.28)

where the matrix elements are given explicitly by (6.21), (6.22) and

$$\mathcal{J}_{\alpha_1\alpha_1}(q) = \mathcal{J}_{\beta_1\beta_1}(q) = \mathcal{J}_{\alpha_2\alpha_2}(q) = \mathcal{J}_{\beta_2\beta_2}(q) = 2\mathcal{J}_2' \left[\cos 2\pi q_x + \cos 2\pi q_y\right] \quad (6.29)$$

Diagonalization of the matrix (6.28) gives

$$\lambda_{1,2}(q) = 2\mathcal{J}_{2}'(\cos 2\pi q_{x} + \cos 2\pi q_{y}) + 2\mathcal{J}_{1}\left[\cos^{2}\pi q_{x} + \cos^{2}\pi q_{y} \pm 2\cos \pi q_{x}\cos \pi q_{y}\left(1 - 2\cos^{2}\frac{\pi}{2}q_{z}\right)\right]^{\frac{1}{2}}$$

$$\lambda_{3,4}(q) = 2\mathcal{J}_{2}'(\cos 2\pi q_{x} + \cos 2\pi q_{y}) -2\mathcal{J}_{1}\left[\cos^{2}\pi q_{x} + \cos^{2}\pi q_{y} \pm 2\cos \pi q_{x}\cos \pi q_{y}\left(1 - 2\cos^{2}\frac{\pi}{2}q_{z}\right)\right]^{\frac{1}{2}}$$
(6.30)

From (6.27) we now have the constraint that $\mathcal{J}_1 + \mathcal{J}'_2 = 0.177$ meV. Figures 6.18 to 6.20 illustrate the dispersion of $\lambda_i(q)$ (i = 1...4) calculated from (6.30) for the ΓN , XZ and ΓX directions in reciprocal space as a function of the magnitude and sign of the exchange interaction parameters \mathcal{J}_1 and \mathcal{J}'_2 . Along ΓZ the nature of the magnetic dispersion remains unchanged from that of the nearest neighbour calculation.

The magnetic dispersion curves of Figures 6.18 to 6.20 clearly show that for positive exchange interaction parameters \mathcal{J}_1 and \mathcal{J}'_2 the maxima of the $\lambda(q)$ occur for $q_m = 0$ and thus the magnetic ordering in the CeSi_x system may be ferromagnetic with the possibility of latent antiferromagnetism. Alternatively, taking the dispersion along ΓX as one example, then for the situation where the next-nearest exchange parameter \mathcal{J}'_2 is negative, Fig. 6.21 illustrates the magnetic propagation vector q_m by which the exchange interaction energy of CeSi_x will be minimized. For small negative values of \mathcal{J}'_2 the dominant magnetic order in the CeSi_x system will remain ferromagnetic but the existence of antiferromagnetic correlations due to magnetic excitations within the system is possible. However, as this parameter becomes more negative and the ratio $|\mathcal{J}'_2|/\mathcal{J}_1$ exceeds 0.25, an incommensurate magnetic order is to be expected.

Using our knowledge of the magnetic dispersion in CeSi_x , it is possible to make an estimate of the variation in the ground state magnetic order of CeSi_x as a function of x. To do this, with the assumption that the cerium 4f electrons are unaffected by the presence of silicon vacancies, it is only necessary to estimate the effect of the silicon concentration x on the cerium-cerium distances and conduction electron density in CeSi_x . The variation in the magnitudes of the exchange interaction parameters \mathcal{J}_1 and \mathcal{J}'_2 may then be calculated within RKKY theory, as shown below.

Calculation of \mathcal{J}_1 and \mathcal{J}'_2 within RKKY theory

As discussed in § 2.3 the dominant exchange interactions in CeSi_x are indirect exchange interactions via a polarization of the conduction electrons. Within the RKKY



Figure 6.18: The eigenvalues $\lambda_i(q)$ (i = 1, ..., 4) calculated for nearest and next-nearest exchange along ΓN for a range of relative magnitudes of the parameters \mathcal{J}_1 and \mathcal{J}'_2 .



Figure 6.19: The eigenvalues $\lambda_i(q)$ (i = 1, ..., 4) calculated for nearest and next-nearest exchange along XZ for a range of relative magnitudes of the parameters \mathcal{J}_1 and \mathcal{J}'_2 (as before a direct path is followed in reciprocal space from the point X to the point Z and the wavevector q is measured from the point X).



Figure 6.20: The eigenvalues $\lambda_i(q)$ (i = 1, ..., 4) calculated for nearest and next-nearest exchange along ΓX for a range of relative magnitudes of the parameters \mathcal{J}_1 and \mathcal{J}'_2 .



Figure 6.21: The variation of the magnetic propagation vector with $|\mathcal{J}'_2|$ for the magnetic dispersion within CeSi_x along ΓX .

theory the conduction electrons are approximated to be 'free-electrons' such that their energy at the Fermi surface is given by

$$E_F = \frac{\hbar^2 k_F^2}{2m_e}$$

and the total number of conduction electrons (having accounted for the spin degeneracy of each k state) per unit volume is

$$Z = \frac{k_F^3}{3\pi^2}$$

RKKY theory gives that the exchange interaction parameter between two spins J_n and J_m , located at positions R_n and R_m , may be calculated by (2.88), i.e.

$$\mathcal{J}_{nm}^{RKKY} = -\frac{m_e(3Z)^{\frac{3}{5}}}{4\hbar^2 \pi^{\frac{1}{5}}} \Gamma^2 (g_J - 1)^2 F\left(2\left(3\pi^2 Z\right)^{\frac{1}{5}} |R_n - R_m|\right)$$

with

$$F(x) = \frac{x\cos x - \sin x}{x^4}$$

and Γ a constant with the dimension of [energy×volume] that is determined by the degree of overlap of the wavefunctions of the s (conduction) and f (localized) electrons.

The results from the neutron powder diffraction refinements of § 3.3, show that at 1.5K the cerium-cerium nearest and next-nearest neighbour distances are respectively

3.99Å and 4.16Å for CeSi_{1.80}, 3.96Å and 4.16Å for the silicon 'poor' phase of CeSi_{1.85}, and 4.08Å and 4.15Å for the CeSi_{1.85} silicon 'rich' phase. In the following calculations, the lattice parameters and ionic separations of the CeSi_{1.85} silicon 'rich' phase will be used for CeSi₂. It is assumed that all cerium ions are in the Ce³⁺ ionization state, irrespective of changes in the silicon concentration, x. Each cerium ion has one localized 4f electron and thus $g_J = \frac{6}{7}$. Defining Z_{cell} to be the total number of conduction electrons per crystallographic unit cell,

$$Z_{cell} = a. \left(b \times c\right) Z \tag{6.31}$$

then Figures 6.22 and 6.23 illustrate the Z_{cell} dependence of \mathcal{J}_1 and \mathcal{J}'_2 calculated from equations (2.88) and (6.31) for CeSi₂ and CeSi_{1.80}. The constant Γ is taken to be in units of Jm³. From these figures it is observed that the nearest neighbour (\mathcal{J}_1) and next-nearest neighbour (\mathcal{J}'_2) exchange interaction coefficients are more similar in their dependence on Z_{cell} for CeSi₂ than for CeSi_{1.80}. For CeSi₂ the functions $\mathcal{J}_1(Z_{cell})$ and $\mathcal{J}'_2(Z_{cell})$ are zero for $Z_{cell} = 1.370$ and $Z_{cell} = 1.308$ respectively. For CeSi_{1.80} the two functions are respectively zero for $Z_{cell} = 1.436$ and $Z_{cell} = 1.270$. Thus for CeSi_{1.80} there is a greater range in Z_{cell} for which the $\mathcal{J}_1(Z_{cell})$ and $\mathcal{J}'_2(Z_{cell})$ exchange interaction coefficients will differ in sign.

The approximation in the RKKY theory that the conduction electrons may be considered as 'free-electrons' has the consequence that the Fermi surface of the system is assumed to be spherical. Approximating the Brillouin zone for a tetragonal crystallographic unit cell of CeSi₂ to be spherical with an average radius of

$$k_{BZ} \approx \frac{\frac{\pi}{a} + \frac{\pi}{a} + \frac{\pi}{c}}{3}$$

then

$$k_{BZ} \approx 0.58 \quad \text{\AA}^{-1} \tag{6.32}$$

and, strictly speaking, for the spherical Fermi surface to be within the first Brillouin zone we have the constraint that

$$Z_{cell} \le 1.56 \tag{6.33}$$



Figure 6.22: \mathcal{J}_1 (solid line) and \mathcal{J}'_2 (broken line) for CeSi₂, calculated within RKKY theory as a function of the number of conduction electrons per crystallographic unit cell.



Figure 6.23: \mathcal{J}_1 (solid line) and \mathcal{J}'_2 (broken line) for CeSi_{1.80}, calculated within RKKY theory as a function of the number of conduction electrons per crystallographic unit cell.

The magnetic ground state of CeSi_x (1.60 $\leq x \leq$ 2.00) as a function of x

In the absence of quantitative electronic band-structure calculations, the variation of the conduction electron density and correspondingly the exchange interaction coefficients with decreasing x may only be discussed qualitatively. The assumption carried over from the discussions of § 6.1 and § 6.2 is that with increasing silicon vacancies (i.e. decreasing x) both the electronic band filling of the anti-bonding π^* -band and the conduction electron band decreases. Hence, the conduction electron density per unit cell (Z_{cell}) decreases with decreasing x.

It is proposed that $\operatorname{CeSi}_x(1.80 \leq x \leq 2.00)$ samples with paramagnetic ground states have a conduction electron density per unit cell in the range $\approx 1.40 \leq Z_{cell} \leq \approx 1.56$. For such a situation, both exchange interaction coefficients \mathcal{J}_1 and \mathcal{J}'_2 are negative and the energy of the system would be minimized by an antiferromagnetic ordering of the cerium magnetic moments. However, as may be seen from Fig. 6.24, the arrangement of cerium ions within the cerium sublattice will lead to frustration effects when both \mathcal{J}_1 and \mathcal{J}'_2 are negative. Assuming a 'spin up' state for the cerium magnetic moment at the origin of the unit cell, there will be frustration between the magnetic moments of the ions in the α'_1 and β_1 positions. It is proposed that such frustration effects may be the cause responsible for the surpression of a magnetically ordered ground state in $\operatorname{CeSi}_x(1.80 \leq x \leq 2.00)$ samples. The existence of magnetic excitations in such samples that are antiferromagnetic in nature may be understood within this framework.

With decreasing silicon concentration and a corresponding decrease in Z_{cell} , it is argued that a situation will eventually be encountered in which the nearest neighbour exchange coefficient \mathcal{J}_1 becomes positive whilst the next-nearest neighbour exchange coefficient \mathcal{J}'_2 is negative. If the ratio $\frac{|\mathcal{J}'_2|}{|\mathcal{J}_1|}$ is small, it may be expected that frustration effects will no longer surpress the formation of a magnetically ordered ground state. As discussed previously, in such a situation the magnetic order in the CeSi_x system will be characterized by the magnetic propagation vector $q_m = 0$ and the order will be predominately ferromagnetic in nature with the possibility of latent antiferromag-


Figure 6.24: a) Illustration of the magnetic frustration within the cerium sublattice of CeSi_x when both the nearest (\mathcal{J}_1) and next-nearest (\mathcal{J}'_2) exchange interaction coefficients are negative. b) The solid and dashed lines indicate the type of exchange interaction parameter characterizing the exchange interaction between the cerium ions shown.

netism and antiferromagnetic correlations at higher temperatures due to magnetic excitations.

With a further decrease in the silicon concentration x and Z_{cell} , the situation where both \mathcal{J}_1 and \mathcal{J}'_2 are positive will be approached. There, the energy of the system will be minimized by a ferromagnetic ordering of the cerium magnetic moments, once again with the possibility of a modulation of the ordered moments due to the occurrence of latent antiferromagnetism. It is proposed that the absence of magnetic correlations within the paramagnetic CeSi_{1.80} (NF) sample (§ 3.6) could be the consequence of both of the coefficients \mathcal{J}_1 and \mathcal{J}'_2 being accidentally close to zero. The ideas presented above are both qualitative and speculative but they do enable many of the features of the magnetic phase diagram of CeSi_x (Fig. 5.3) to be understood.

In summary, the determination of the magnetic dipersion curves of CeSi_x for nearest and next-nearest neighbour exchange between cerium ions on the tetragonal ThSi₂-type lattice are sufficient for our purposes and for the discussion of how the ground state magnetic order of CeSi_x will vary as a function of the corresponding exchange interaction coefficients. Retaining the assumption proposed in § 6.2 that the conduction electron density of CeSi_x decreases with increasing silicon vacancies, both the existence of antiferromagnetic correlations in the paramagnetic state of $\operatorname{CeSi}_x (1.80 \leq x \leq 2.00)$ samples and the non-magnetic \rightarrow magnetic ground state phase transition as a function of x may be understood. Both phenomena occur due to the variation of the nearest and next-nearest neighbour exchange interaction coefficients due to the decrease in the conduction electron density of states of CeSi_x with decreasing x. In conclusion, it is proposed that the non-magnetic \rightarrow magnetic phase transition in CeSi_x is neither related to any change in the valence state of the cerium ions nor caused by a 'dense' Kondo effect but is solely the result of the variation of the conduction electron density of the introduction of silicon vacancies into the CeSi_2 lattice.

Chapter 7

Conclusions

Following on from the experimental work that has been performed and reviewed within this thesis, the proposed structural and magnetic phase diagrams of the rareearth metallic alloy $\operatorname{CeSi}_x(1.60 \le x \le 2.00)$ are illustrated in Figures 7.1 and 7.2. These diagrams show how the CeSi_x system undergoes a variety of structural and magnetic phase transitions both as a function of temperature and silicon concentration. They also highlight the current uncertainties in the critical temperatures and silicon concentrations that define the boundaries between the different regions of the phase diagram.

The neutron and X-ray synchrotron powder diffraction experiments and SEM experiments that have been described in Chapter 3 provide evidence for the crystallographic instability of $\text{CeSi}_{1,80}$ and $\text{CeSi}_{1,85}$ samples with the ThSi₂-type crystal structure. Coupled with the experimental observations reviewed in Chapter 4, it is proposed that the crystallographic instability of CeSi_x samples with the ThSi₂-type structure extends over the concentration range $1.80 \leq x \leq 2.00$. For samples in the silicon concentration range $1.80 \leq x \leq \approx 1.90$, a reversible low temperature phase separation has been observed into two Ce-Si phases with different proportions of silicon vacancies. Within the phase with the larger proportion of vacancies there is an orthorhombic distortion of the crystallographic unit cell to the GdSi₂-type structure and a preferential ordering of the vacancies onto one of the two inequivalent silicon lattice sites. The critical temperature defining the phase separation (T_{cs}) has been



Figure 7.1: Schematic illustration of the proposed structural phase diagram of CeSi_x (1.60 $\leq x \leq 2.00$).



Figure 7.2: Schematic illustration of the proposed magnetic phase diagram of CeSi_x (1.60 $\leq x \leq 2.00$).

observed to be $100K \leq T_{cs} \leq 200K$ for CeSi_{1.80} (NF) and $T_{cs} > 300K$ for CeSi_{1.85}. The ratio of the two phases coexisting within the samples below T_{cs} is temperature dependent.

The experiments described in Chapter 3 have illustrated the subtle nature of the temperature dependent structural phase transition within $\operatorname{CeSi}_x(1.80 \leq x \leq \approx 1.90)$ samples, such that it may only be observed by very high resolution diffraction experiments. It is remarked that, in future, only high resolution experiments will be sufficient to clarify the exact range of silicon concentration for which there is a coexistence of two phases at low temperatures (i.e. x_{cs} and x'_{cs}) and the exact temperature dependence of the relative proportion of these two phases.

The preparation of $\operatorname{CeSi}_{1.80}$ samples with different crystal structures and magnetic ground states ($\operatorname{CeSi}_{1.80}(F)$ and $\operatorname{CeSi}_{1.80}(NF)$) have illustrated the importance of sample preparation and heat treatment on the crystallographic and magnetic properties of CeSi_x . The close correspondence between the critical silicon concentrations x_{cs} (that defines the boundary between crystallographically stable CeSi_x samples with the GdSi_2 -type crystal structure and CeSi_x samples that have the ThSi_2 -type structure at high temperatures and for which a low temperature phase separation occurs) and x_c (that defines the boundary between CeSi_x samples with magnetically ordered or paramagnetic ground states) is repeatedly observed throughout Chapters 3 and 4. It appears that the orthorhombic GdSi_2 -type structure that is only found for silicon deficient CeSi_x samples is a necessary condition for the formation of a magnetically ordered ground state. Further high resolution experiments are required on a series of CeSi_x samples within the concentration range $(1.75 \leq x \leq 1.85)$ in order to confirm this interpretation.

The unambiguous determination of the paramagnetic scattering from CeSi_{1.80} (F), CeSi_{1.80} (NF) and CeSi_{1.85} samples using spin polarized neutrons and neutron spin polarization analysis has shown that for CeSi_{1.80} (F), a stable single phase sample with the GdSi₂-type crystal structure, the paramagnetic scattering contribution at 300K is of the magnitude expected taking into account the effect of the crystalline electric-field. The enhancement of the average paramagnetic scattering intensity at 13K, above that expected due to the CEF, may possibly be the result of a critical magnetic scattering contribution within the sample which is just above $T_c = 12.5$ K. For the CeSi_{1.80} (NF) sample that undergoes a phase separation below 200K into two Ce-Si phases with different proportions of silicon vacancies, the paramagnetic differential scattering cross section at 1.5K, 30K and 100K resembles that of a perfect paramagnet. However, the magnitude of the paramagnetic scattering intensity is reduced compared to that expected on the basis of the crystalline electric-field by an average factor of three at all temperatures measured. The CeSi_{1.85} sample also exhibits a low temperature phase separation and has a paramagnetic ground state but its paramagnetic differential scattering cross section is strikingly different from that of $CeSi_{1,80}$ (NF). The paramagnetic scattering intensity at low temperatures is of the order expected taking into consideration the effects of the crystalline electricfield. However, at higher temperatures the paramagnetic scattering is significantly enhanced above that expected and antiferromagnetic correlations are observed, the magnitude of which increase with increasing temperature. While the existence of such antiferromagnetic correlations in CeSi_{1.85} and the absence of magnetic correlations in $CeSi_{1.80}$ (NF) can be understood within the framework of the ideas proposed in Chapter 6, the reduction of the paramagnetic scattering intensity of CeSi_{1.80} (NF) below that expected taking into account the effect of the crystalline electric-field, remains to be explained.

The discussions described in Chapters 5 and 6 have been an attempt to gain a better understanding of the observed structural and magnetic behaviour of CeSi_x (1.60 $\leq x \leq 2.00$) and the physical mechanisms influencing such behaviour and the structural and magnetic phase transitions as a function of temperature and x. In Chapter 5, firstly from a thermodynamic viewpoint, the conditions have been discussed under which a low temperature phase separation in CeSi_x (1.80 $\leq x \leq \approx 1.90$) samples into two phases with an unequal proportion of silicon vacancies will cause a minimization of the free energy of the system. Subsequently, the Landau theory of phase transitions has been applied to the CeSi_x system to determine the possible types of temperature dependent structural and magnetic phase transitions that can occur, subject to the known symmetries of the high and low temperature phases, within a silicon 'poor' CeSi_x (1.80 $\leq x \leq \approx 1.90$) phase and CeSi_x ($x \leq 1.80$) respectively. For the structural phase transitions from an initial high temperature phase

with the ThSi₂-type crystal structure, if the phenomenon of silicon vacancy ordering or an orthorhombic distortion occur on their own, the structural phase transition is of second-order. In the situation where both the vacancy ordering and orthorhombic distortion occur simultaneously, the effect of the coupling is to renormalize the phase transition temperature; there still exists a continuous second-order phase transition. As for the temperature dependent magnetic phase transiton within CeSi_x ($x \leq 1.80$) samples that have the orthorhombic GdSi₂-type structure both above and below the transition temperature, symmetry dictates that in the presence of a ferromagnetically ordered ground state due to the magnetic exchange interactions between the cerium ions, there will always exist the possibility of an induced antiferromagnetically ordered component. Such a component is the result of relativistic spin-spin and spin-orbit interactions and is coupled collinearly to the ferromagnetic component. As relativistic interactions are weaker than exchange force interactions, the effect of this coupling will be to produce a weak modulation of the ferromagnetically ordered moments, as has been observed experimentally (Sato *et al.*, 1985).

A speculative discussion has been performed that proposes a physical mechanism for the observed crystallographic instability of CeSi_x (1.80 $\leq x \leq 2.00$) samples with the ThSi₂-type crystal structure and subsequently an explanation for the observed structural and magnetic phase transitions in CeSi_x as a function of the silicon concentration, x. The starting point on which this discussion has been based is the observation of a similar temperature dependent structural phase transition within PrSi₂ and silicon concentration dependent structural and magnetic phase transitions in $\text{CeSi}_{2-x}\text{Ga}_x$ (0.2 < x < 0.5). From these observations it is proposed that the crystallographic instability of CeSi_x (1.80 $\leq x \leq 2.00$) samples is not related to changes in the valence state of the cerium ions and a subsequent variation of the cerium ionic radius, but rather is significantly influenced by the electronic configuration and bonding of the non-metal atoms (Si, Ga) within the silicon sublattice. The concept of molecular orbital theory has been used to illustrate why the GdSi₂-type structure of silicon deficient $\operatorname{CeSi}_x(x \leq 1.80)$ samples would be energetically more favourable than the ThSi₂-type structure of CeSi₂. The introduction of vacancies into the silicon sublattice of CeSi₂ enables the Coulomb interaction energy due to the overlap of the 3p electron wavefunctions of neighbouring silicon atoms to be reduced; i.e. within the notation of molecular orbital theory the presence of silicon vacancies results in a reduction in the band filling of the anti-bonding π^* -band. The ideas presented have been shown to be consistent with the observed orthorhombic distortion of CeSi_x ($x \leq 1.80$) samples. In addition, the elementary electron counting schemes performed suggest a possible explanation for the observed enhancement of the linear coefficient $\gamma(x)$ of the electronic specific-heat capacity as a function of xthat is independent of the cerium 4f electrons and the phenomenon of intermediate valency. In this case, the enhancement is suggested to be the result of the approach of the Fermi level to the bottom of the anti-bonding π^* -band with decreasing x and the corresponding increase in the electronic density of states at the Fermi level.

The ideas above have been extended to a qualitative discussion of the electronic band-structure of CeSi_{x} . It has been proposed that the introduction of silicon vacancies causes a decrease in the conduction electron density of CeSi_x with decreasing x. In the absence of quantitative electronic band-structure calculations the discussions remain highly speculative. However, using them to discuss the effect of silicon concentration on the magnitude and sign of the exchange interaction coefficients between the cerium ions within RKKY theory, the discussions are able to provide consistent explanations for many of the features observed within the magnetic phase diagram of CeSi_{x} . From the calculation of the magnetic dispersion within CeSi_{x} for nearest and next-nearest neighbour exchange interactions, then for CeSi_x (1.80 $\leq x \leq 2.00$) samples for which it is proposed that both the nearest (\mathcal{J}_1) and next-nearest (\mathcal{J}'_2) neighbour exchange interaction coefficients are negative, it is also proposed that frustration effects prevent the formation of an antiferromagnetically ordered magnetic ground state. Such an explanation would be consistent with the observation of magnetic excitations within a paramagnetic CeSi_{1.85} sample that are antiferromagnetic in nature (as observed in § 3.6). With a further decrease in the silicon concentration x and the conduction electron density of $CeSi_x$, it may be logically expected that a situation will be eventually encounterd in which \mathcal{J}_1 is positive and \mathcal{J}_2' is either small in magnitude and negative, or also positive. In such cases, frustration effects would no longer prevent the formation of a magnetically ordered ground state and the non-magnetic \rightarrow magnetic phase transition with decreasing x may be understood. Furthermore, if frustration effects are responsible for the supression of a magnetically ordered ground state in CeSi_x samples with the ThSi_2 -type structure, it may be understood why the occurrence of a crystallographic distortion to the GdSi_2 -type structure appears to be of importance for the formation of a magnetically ordered ground state.

It must be remarked that the ideas presented above can neither account for the reduction in the paramagnetic scattering intensity of CeSi_{1.80} (NF) at low temperatures, nor the reduction in the observed magnetic moment of $CeSi_{1.80}$ (F) and the $\operatorname{CeSi}_{x}(x \leq 1.80)$ samples of Sato et al. (1985), Pierre et al. (1990a) and Yashima et al. (1982b). Previously, it has been these observations, coupled with the observation from measurements of the electronic specific-heat capacity of a reduced magnetic entropy of $\operatorname{CeSi}_x(x \leq 1.80)$ samples below T_c compared to the $R \ln 2$ contribution expected for a ground state doublet (Yashima et al., 1982b) and the type '1' temperature dependence of the electrical resistivity of CeSi_x ($x \leq 1.80$) samples (§ 4.5) in which there is a minimum in ρ , that has invoked attempts to explain the behaviour of the CeSi_x system with a 'dense' Kondo model (Yashima et al., 1982b). The authors propose that for the ferromagnetic CeSi_x ($x \leq 1.80$) samples the sublattice of cerium ions orders ferromagnetically via the RKKY interaction while the Kondo effect reduces the magnetic moment per ion. Furthermore, they attribute the nonmagnetic \rightarrow magnetic ground state phase transition in CeSi_x as a function of x to the domination of the Kondo effect, whereby the formation of bound states between the conduction electrons and the cerium ions in which the former align antiferromagnetically to the cerium magnetic moment and compensate the spin, results in the bound states having no resultant magnetic moment that may be aligned via the RKKY interaction. While the discussions presented within this thesis do propose an increase in the conduction electron density of CeSi_x with increasing x that would be consistent with an increased Kondo effect causing a non-magnetic ground state for $x \rightarrow 2.00$, it is argued here that alternative mechanisms do also account for this transition. It is stressed that the structural phase transitions and distortions of the crystal lattice are clearly of importance in relation to the magnetic phase transitions in CeSi_x and must be investigated further in order to clarify the the dominant mechanisms that determine the magnetic behaviour of $CeSi_x$.

In conclusion, the hypothesis that the conduction electron density in CeSi_x decreases with decreasing x provides a consistent explanation for the non-magnetic \rightarrow

magnetic phase transition within CeSi_x with decreasing x due to the corresponding variation of the exchange interaction coefficients. The absence of a magnetically ordered ground state for CeSi_x (1.80 $\leq x \leq 2.00$) samples with the ThSi₂-type structure is considered to be due to the effect of frustration of the cerium magnetic moments that are trying to align antiferromagnetically. Throughout these discussions the cerium 4f electrons have been considered to remain well localized around the cerium ions. It is proposed that neither the structural nor magnetic phase transitions in CeSi_x as a function of temperature or silicon concentration, nor the observed enhancement of the linear coefficient of the electronic specific-heat capacity as a function of x, are related to the intermediate valency of the cerium 4f electrons. Furthermore, an explanation is provided for the non-magnetic \rightarrow magnetic ground state phase transition as a function of x that is independent of the Kondo effect. The discussions presented within this thesis have proposed alternative explanations for such phenomena, and though these are speculative, the observation of phase separations, silicon vacancy ordering, crystal distortions and the close proximity of x_c and x_{cs} clearly support that the lattice degrees of freedom are of importance in determining the magnetic ground state properities of CeSi_x.

In future work, high resolution diffraction experiments and theoretical electronic band-structure calculations will be necessary in order to pursue the ideas and suggestions presented within this thesis. Such work will enable the structural and magnetic phase diagrams of $\operatorname{CeSi}_x(1.60 \leq x \leq 2.00)$ to be completed and allow the coupling between the occurrence of the structural and magnetic phase transitions as a function of silicon concentration to be more fully understood. In addition, an investigation of the magnon dispersion of single crystal CeSi_x samples by neutron scattering would provide information concerning the variation of the exchange interaction coefficients as a function of x, and provide experimental proof or a contradiction of the ideas presented here. For the present time, it is hoped that this investigation has contributed to the understanding of the physical behaviour of the rare-earth metallic alloy CeSi_x and will provide a useful starting point for future investigations.

Appendix A

Transformation of the strain tensor under the symmetry operations of the point group 4/mmm

The transformation of the components of a second rank tensor $[\epsilon]$ from one orthogonal set of axes Ox_i to another set Ox'_i is given by

	x 1	X 2	x3
_x'_1	a ₁₁	a ₁₂	a ₁₃
\mathbf{x}_{2}^{\prime}	a ₂₁	a22	a ₂₃
x'3	a ₃₁	a ₃₂	a33

The coefficients a_{ij} are known as the direction cosines (Nye, 1967). The strain tensor transformation can be expressed as

$$[\epsilon'_{ij}] = [a_{ip}][\epsilon_{pq}][a_{qj}]$$

Identity operator \hat{E}

For this operator the direction cosines a_{ij} are given by

$$a_{ij} = \begin{cases} 1 \quad (i=j) \\ 0 \quad (i\neq j) \end{cases} \implies \hat{E}[\epsilon] = \begin{vmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{vmatrix}$$

 \hat{C}_{4z}^+ (positive fourfold rotation about the z axis)

For a positive rotation where $x \to -y, y \to x$, the transformation tensor [a] is given by

$$[a] = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \Rightarrow \hat{C}^+_{4z}[\epsilon] = \begin{bmatrix} \epsilon_{yy} & -\epsilon_{yz} & -\epsilon_{yz} \\ -\epsilon_{xy} & \epsilon_{xz} & \epsilon_{xz} \\ -\epsilon_{zy} & \epsilon_{zx} & \epsilon_{zz} \end{bmatrix}$$

\hat{C}_{4z}^- (negative fourfold rotation about the z axis)

For a negative rotation where $x \to y, y \to -x$, the transformation tensor [a] is given by

$$[a] = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \Rightarrow \hat{C}_{4z}^{-}[\epsilon] = \begin{bmatrix} \epsilon_{yy} & -\epsilon_{yz} & \epsilon_{yz} \\ -\epsilon_{xy} & \epsilon_{xx} & -\epsilon_{xz} \\ \epsilon_{zy} & -\epsilon_{zx} & \epsilon_{zz} \end{bmatrix}$$

\hat{C}_{2z} (twofold rotation about the z axis)

The transformation tensor [a] is given by

$$[a] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \Rightarrow \hat{C}_{2z}[\epsilon] = \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & -\epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & -\epsilon_{yz} \\ -\epsilon_{zx} & -\epsilon_{zy} & \epsilon_{zz} \end{bmatrix}$$

 \hat{C}_{2x} (twofold rotation about the x axis)

The transformation tensor [a] is given by

$$[a] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \Rightarrow \hat{C}_{2x}[\epsilon] = \begin{bmatrix} \epsilon_{xx} & -\epsilon_{xy} & -\epsilon_{xz} \\ -\epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ -\epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix}$$

 \hat{C}_{2y} (twofold rotation about the y axis)

The transformation tensor [a] is given by

$$[a] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \Rightarrow \hat{C}_{2y}[\epsilon] = \begin{bmatrix} \epsilon_{xx} & -\epsilon_{xy} & \epsilon_{xz} \\ -\epsilon_{yx} & \epsilon_{yy} & -\epsilon_{yz} \\ \epsilon_{zx} & -\epsilon_{zy} & \epsilon_{zz} \end{bmatrix}$$

\hat{C}_{2xy} (twofold rotation about an axis that bisects the x and y axis)

The transformation tensor [a] is given by

$$[a] = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \Rightarrow \hat{C}_{2xy}[\epsilon] = \begin{bmatrix} \epsilon_{yy} & \epsilon_{yx} & -\epsilon_{yz} \\ \epsilon_{xy} & \epsilon_{xx} & -\epsilon_{xz} \\ -\epsilon_{zy} & -\epsilon_{zx} & \epsilon_{zz} \end{bmatrix}$$

 $\hat{C}_{2\bar{x}y}$ (twofold rotation about an axis that bisects the -x and y axis)

The transformation tensor [a] is given by

$$\begin{bmatrix} a \end{bmatrix} = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \Rightarrow \hat{C}_{2\bar{x}y}[\epsilon] = \begin{bmatrix} \epsilon_{yy} & \epsilon_{yx} & \epsilon_{yz} \\ \epsilon_{xy} & \epsilon_{xx} & \epsilon_{xz} \\ \epsilon_{zy} & \epsilon_{zx} & \epsilon_{zz} \end{bmatrix}$$

Inversion operator \hat{I}

The transformation tensor [a] is given by

$$[a] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \Rightarrow \hat{I}[\epsilon] = \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix}$$

 \hat{S}_{4z}^+ (positive fourfold rotation about the z axis followed by a reflection in the xy plane)

For a positive rotation where $x \to -y, y \to x$, the transformation tensor [a] is given by

$$[a] = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \Rightarrow \hat{S}^+_{4z}[\epsilon] = \begin{bmatrix} \epsilon_{yy} & -\epsilon_{yz} & \epsilon_{yz} \\ -\epsilon_{xy} & \epsilon_{xx} & -\epsilon_{xz} \\ \epsilon_{zy} & -\epsilon_{zx} & \epsilon_{zz} \end{bmatrix}$$

 \hat{S}_{4z}^- (negative fourfold rotation about the z axis followed by a reflection in the xy plane)

For a negative rotation where $x \to y, y \to -x$, the transformation tensor [a] is given by

$$[a] = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \Rightarrow \hat{S}_{4z}^{-}[\epsilon] = \begin{bmatrix} \epsilon_{yy} & -\epsilon_{yx} & -\epsilon_{yz} \\ -\epsilon_{xy} & \epsilon_{xx} & \epsilon_{xz} \\ -\epsilon_{zy} & \epsilon_{zx} & \epsilon_{zz} \end{bmatrix}$$

 $\hat{\sigma}_z$ (reflection in the xy plane)

The transformation tensor [a] is given by

$$[a] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \Rightarrow \hat{\sigma}_{z}[\epsilon] = \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & -\epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & -\epsilon_{yz} \\ -\epsilon_{zx} & -\epsilon_{zy} & \epsilon_{zz} \end{bmatrix}$$

$\hat{\sigma}_x$ (reflection in the yz plane)

The transformation tensor [a] is given by

$$[a] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \Rightarrow \hat{\sigma}_x[\epsilon] = \begin{bmatrix} \epsilon_{xx} & -\epsilon_{xy} & -\epsilon_{xz} \\ -\epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ -\epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix}$$

 $\hat{\sigma}_y$ (reflection in the xz plane)

The transformation tensor [a] is given by

$$[a] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \Rightarrow \hat{\sigma}_{y}[\epsilon] = \begin{bmatrix} \epsilon_{xx} & -\epsilon_{xy} & \epsilon_{xz} \\ -\epsilon_{yx} & \epsilon_{yy} & -\epsilon_{yz} \\ \epsilon_{zx} & -\epsilon_{zy} & \epsilon_{zz} \end{bmatrix}$$

$\hat{\sigma}_{xy}$ (reflection in the of the z axis and the bisector of the x and y axes)

The transformation tensor [a] is given by

$$[a] = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \Rightarrow \hat{\sigma}_{xy}[\epsilon] = \begin{bmatrix} \epsilon_{yy} & \epsilon_{yx} & \epsilon_{yz} \\ \epsilon_{xy} & \epsilon_{xx} & \epsilon_{xz} \\ \epsilon_{xy} & \epsilon_{zx} & \epsilon_{zz} \end{bmatrix}$$

 $\hat{\sigma}_{xy}$ (reflection in the of the z axis and the bisector of the -x and y axes)

The transformation tensor [a] is given by

$$[a] = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \Rightarrow \hat{\sigma}_{\bar{x}y}[\epsilon] = \begin{bmatrix} \epsilon_{yy} & \epsilon_{yx} & -\epsilon_{yz} \\ \epsilon_{xy} & \epsilon_{xx} & -\epsilon_{xz} \\ -\epsilon_{zy} & -\epsilon_{zx} & \epsilon_{zz} \end{bmatrix}$$

Comparison of the transformations on the strain tensor under the symmetry operations of 4/mmm

From the transformations above it can be seen that, as expected :-

$$\begin{array}{cccc} \hat{E} & \equiv & \hat{I} \\ \hat{C}^+_{4z} & \equiv & \hat{S}^-_{4z} \\ \hat{C}^-_{4z} & \equiv & \hat{S}^+_{4z} \\ \hat{C}_{2z} & \equiv & \hat{\sigma}_z \\ \hat{C}_{2x} & \equiv & \hat{\sigma}_x \\ \hat{C}_{2y} & \equiv & \hat{\sigma}_y \\ \hat{C}_{2xy} & \equiv & \hat{\sigma}_{xy} \\ \hat{C}_{2xy} & \equiv & \hat{\sigma}_{xy} \\ \hat{C}_{2\bar{x}y} & \equiv & \hat{\sigma}_{xy} \end{array}$$

Projection of the strain tensor $[\epsilon]$ onto the irreducible spaces associated to the crystallographic point group 4/mmm

Table 7.1 has been reproduced from Koster *et al.* (1963). The alternative labels of the representations in parenthesis follow the notation of Mulliken (1933) and are consistent with the notation used in Bradley and Cracknell (1972). The crystal symmetry operations are defined as follows:-

\hat{E}	identity operation
\hat{C}^+_{4z}	positive fourfold rotation about the z axis
\hat{C}_{2z}	twofold rotation about the z axis
\hat{C}_{2x}	twofold rotation about the x axis
\hat{C}_{2y}	twofold rotation about the y axis
\hat{C}_{2xy}	twofold rotation about the axis that bisects the x
	and y axes
$\hat{C}_{2\bar{x}y}$	twofold rotation about the axis that bisects the $-x$
	and y axes
Î	inversion operation
\hat{S}^+_{4z}	positive fourfold rotation about the z axis followed
	by a reflection in the xy plane
$\hat{\sigma}_{z}$	reflection in a plane perpendicular to the z axis
$\hat{\sigma}_{x}$	reflection in the yz plane
$\hat{\sigma}_y$	reflection in the xz plane
$\hat{\sigma}_{xy}$	reflection in a plane containing the z axis and the
	axis that bisects the x and y axes
$\hat{\sigma}_{\bar{x}y}$	reflection in a plane containing the z axis and the
	axis that bisects the $-x$ and y axes

The projection operator used to determine the projection of an arbitrary function onto the space associated with the irreducible representation Γ_{ι} of \tilde{G}_0 has been defined

		Ê	\hat{C}^+_{4z}	Ĉ22	\hat{C}_{2x}	\hat{C}_{2xy}	Î	\hat{S}_{4z}^{+}	σ,	$\hat{\sigma}_x$	$\hat{\sigma}_{xy}$
			\hat{C}_{4z}^{-}		\hat{C}_{2y}	$\hat{C}_{2\#y}$		\hat{S}^{4z}		$\hat{\sigma}_{y}$	σ̂ _{æy}
Γ_1	(A_1)	1	1	1	1	1	1	1	1	1	1
Γ_2	(A_2)	1	1	1	-1	-1	1	1	1	-1	-1
Γ_3	(B_1)	1	-1	1	1	-1	1	-1	1	1	-1
Γ4	(B_2)	1	-1	1	-1	1	1	-1	1	-1	1
Γ_5	(E)	2	0	-2	0	0	2	0	-2	0	0

Table 7.1: Character table for the point group 4/mmm

by equation (5.26),

$$\hat{P}_{\iota} = \frac{l_{\iota}}{d(\tilde{G}_0)} \sum_{\hat{g} \in \tilde{G}_0} \chi_{\iota}^*(\hat{g})\hat{g}$$

where l_i is the dimensionality of the Γ_i , $d(\tilde{G}_0)$ represents the number of symmetry operations $\hat{g} \in \tilde{G}_0$ and $\chi_i^*(\hat{g})$ is the complex conjugate of the character of the symmetry element \hat{g} within the representation Γ_i . The projection of the strain tensor $[\epsilon]$ onto the space associated with the ι^{th} irreducible representation of the group $\tilde{G}_0 = 4/mmm$ is given by

$$[\epsilon]_{\iota} = \hat{P}_{\iota}[\epsilon] \tag{7.1}$$

Using (5.26), (7.1), Table 7.1 and the previous results for the transformation of the strain tensor under $\hat{g} \in \tilde{G}_0$, one obtains:-

Projection on Γ_1

$$\begin{split} [\epsilon]_1 &= \frac{2}{16} \left\{ \hat{E}[\epsilon] + \hat{C}^+_{4z}[\epsilon] + \hat{C}^-_{4z}[\epsilon] + \hat{C}_{2z}[\epsilon] + \hat{C}_{2x}[\epsilon] + \hat{C}_{2y}[\epsilon] + \hat{C}_{2xy}[\epsilon] + \hat{C}_{2\bar{x}y}[\epsilon] \right\} \\ &\Rightarrow [\epsilon]_1 = \frac{1}{2} \begin{pmatrix} \epsilon_{xx} + \epsilon_{yy} & 0 & 0 \\ 0 & \epsilon_{xx} + \epsilon_{yy} & 0 \\ 0 & 0 & 2\epsilon_{zz} \end{pmatrix} \end{split}$$

Projection on Γ_2

$$[\epsilon]_{2} = \frac{2}{16} \left\{ \hat{E}[\epsilon] + \hat{C}^{+}_{4z}[\epsilon] + \hat{C}^{-}_{4z}[\epsilon] + \hat{C}_{2z}[\epsilon] - \hat{C}_{2x}[\epsilon] - \hat{C}_{2y}[\epsilon] - \hat{C}_{2xy}[\epsilon] - \hat{C}_{2xy}[\epsilon] \right\}$$

$$\Rightarrow [\epsilon]_2 = \frac{1}{2} \begin{pmatrix} 0 & \epsilon_{xy} - \epsilon_{yx} & 0 \\ \epsilon_{yx} - \epsilon_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

As the strain tensor is symmetric $\epsilon_{ij} = \epsilon_{ji}$, $\Rightarrow [\epsilon]_2 = 0$.

Projection on Γ_3

$$\begin{split} [\epsilon]_{3} &= \frac{2}{16} \left\{ \hat{E}[\epsilon] - \hat{C}^{+}_{4z}[\epsilon] - \hat{C}^{-}_{4z}[\epsilon] + \hat{C}_{2z}[\epsilon] + \hat{C}_{2x}[\epsilon] + \hat{C}_{2y}[\epsilon] - \hat{C}_{2xy}[\epsilon] - \hat{C}_{2xy}[\epsilon] \right\} \\ &\Rightarrow [\epsilon]_{3} = \frac{1}{2} \begin{pmatrix} \epsilon_{xx} - \epsilon_{yy} & 0 & 0 \\ 0 & \epsilon_{yy} - \epsilon_{xx} & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{split}$$

Projection on Γ_4

$$\begin{split} [\epsilon]_{4} &= \frac{2}{16} \left\{ \hat{E}[\epsilon] - \hat{C}_{4z}^{+}[\epsilon] - \hat{C}_{4z}^{-}[\epsilon] + \hat{C}_{2z}[\epsilon] - \hat{C}_{2x}[\epsilon] - \hat{C}_{2y}[\epsilon] + \hat{C}_{2xy}[\epsilon] + \hat{C}_{2xy}[\epsilon] \right\} \\ &\Rightarrow [\epsilon]_{4} = \frac{1}{2} \begin{pmatrix} 0 & \epsilon_{xy} + \epsilon_{yx} & 0 \\ \epsilon_{yx} + \epsilon_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{split}$$

Since the strain tensor is symmetric,

$$\Rightarrow [\epsilon]_4 = \left(\begin{array}{ccc} 0 & \epsilon_{xy} & 0\\ \epsilon_{yx} & 0 & 0\\ 0 & 0 & 0\end{array}\right)$$

Projection on Γ_5

$$[\epsilon]_5 = \frac{4}{16} \left\{ 2\hat{E}[\epsilon] - 2\hat{C}_{2z}[\epsilon] \right\} \qquad \Rightarrow [\epsilon]_5 = \begin{pmatrix} 0 & 0 & \epsilon_{xz} \\ 0 & 0 & \epsilon_{yz} \\ \epsilon_{xx} & \epsilon_{xy} & 0 \end{pmatrix}$$

From the projections above it may easily be verified that, as expected

$$[\epsilon]_1 + [\epsilon]_2 + [\epsilon]_3 + [\epsilon]_4 + [\epsilon]_5 = [\epsilon]$$

Table 7.2: Transformation of the silicon lattice site probabilities n_1 and n_2 under the symmetry operations $\hat{g} \in \tilde{G}_0$ where $\tilde{G}_0 = 4/mmm$.

Symmetry operation, \hat{g}	$\hat{g}(n_1)$	$\hat{g}(n_2)$
Ê, Î	n_1	n_2
$\hat{C}^+_{4z},\hat{C}^{4z},\hat{S}^+_{4z},\hat{S}^{4z}$	n_2	n_1
$\hat{C}_{2z},\hat{\sigma}_{z}$	n_1	n_2
$\hat{C}_{2x},\hat{C}_{2y},\hat{\sigma}_x,\hat{\sigma}_y$	n_1	n_2
$\hat{C}_{2xy},\hat{C}_{2ar{x}y},\hat{\sigma}_{xy},\hat{\sigma}_{ar{x}y}$	n_2	n_1

Projection of the 'disorder' parameter Δ and the 'total-probability' parameter N onto the irreducible spaces associated to the crystallographic point group 4/mmm

The projections of the disorder parameter Δ and the total-probability parameter N onto the spaces associated with the irreducible representations Γ_{ι} of \tilde{G}_0 have been defined by (5.29) and (5.30), ie.

$$\Delta_{\iota} = n_1^{\iota} - n_2^{\iota}$$

and

$$N_{\iota} = n_1^{\iota} + n_2^{\iota}$$

The transformation properties of n_1 and n_2 (the probabilities of occupation of the two types of silicon lattice sites within the GdSi₂-type structure) under the symmetry operations \hat{g} of the crystallographic point group $\tilde{G}_0 = 4/mmm$ are shown in Table 7.2. Using the projection operator (5.26) and the results of Table 7.2, the projections n_1^t and n_2^t ($\iota = 1, \ldots, 5$) are determined below. Subsequently Δ_{ι} and N_{ι} are calculated from (5.29) and (5.30).

Projection on Γ_1

$$n_{1}^{1} = \frac{2}{16} \left\{ \hat{E}n_{1} + \hat{C}_{4z}^{+}n_{1} + \hat{C}_{4z}^{-}n_{1} + \hat{C}_{2z}n_{1} + \hat{C}_{2x}n_{1} + \hat{C}_{2y}n_{1} + \hat{C}_{2xy}n_{1} + \hat{C}_{2$$

Similarly

$$n_2^1 = \frac{1}{2}(n_2 + n_1)$$

and thus $\Delta_1 = 0$, $N_1 = n_1 + n_2$.

Projection on Γ_2

$$n_{1}^{2} = \frac{2}{16} \left\{ \hat{E}n_{1} + \hat{C}_{4z}^{+}n_{1} + \hat{C}_{4z}^{-}n_{1} + \hat{C}_{2z}n_{1} - \hat{C}_{2x}n_{1} - \hat{C}_{2y}n_{1} - \hat{C}_{2xy}n_{1} - \hat{C}_{2$$

Similarly $n_2^2 = 0$ and thus $\Delta_2 = 0$, $N_2 = 0$.

Projection on Γ_3

$$n_{1}^{3} = \frac{2}{16} \left\{ \hat{E}n_{1} - \hat{C}_{4z}^{+}n_{1} - \hat{C}_{4z}^{-}n_{1} + \hat{C}_{2z}n_{1} + \hat{C}_{2x}n_{1} + \hat{C}_{2y}n_{1} - \hat{C}_{2xy}n_{1} - \hat{C}_{2xy}n_{1} \right\}$$
$$n_{1}^{3} = \frac{1}{8} \left(n_{1} - n_{2} - n_{2} + n_{1} + n_{1} + n_{1} - n_{2} - n_{2} \right) = \frac{1}{2} \left(n_{1} - n_{2} \right)$$

Similarly

$$n_2^3 = \frac{1}{2} (n_2 - n_1)$$

and thus $\Delta_3 = n_1 - n_2$, $N_3 = 0$.

Projection on Γ_4

$$n_{1}^{4} = \frac{2}{16} \left\{ \hat{E}n_{1} - \hat{C}_{4z}^{+}n_{1} - \hat{C}_{4z}^{-}n_{1} + \hat{C}_{2z}n_{1} - \hat{C}_{2x}n_{1} - \hat{C}_{2y}n_{1} + \hat{C}_{2xy}n_{1} + \hat{C}_{2\bar{x}y}n_{1} \right\}$$
$$n_{1}^{4} = \frac{1}{8} \left(n_{1} - n_{2} - n_{2} + n_{1} - n_{1} - n_{1} + n_{2} + n_{2} \right) = 0$$

Similarly $n_2^4 = 0$ and thus $\Delta_4 = 0$, $N_4 = 0$.

,

Projection on Γ_5

$$n_{1}^{5} = \frac{4}{16} \left\{ 2\hat{E}n_{1} - 2\hat{C}_{2z}n_{1} \right\}$$
$$n_{1}^{5} = \frac{1}{4} \left(2n_{1} - 2n_{1} \right) = 0$$

•

Similarly $n_2^5 = 0$ and thus $\Delta_5 = 0$, $N_5 = 0$.

Appendix B

Symmetries of the possible magnetically ordered phases in $CeSi_x$ ($x \leq 1.80$)

For the temperature dependent phase transition from a paramagnetic to a magnetically ordered state in $\operatorname{CeSi}_x(x \leq 1.80)$ samples with the GdSi_2 -type crystal structure, the magnetic point group characterizing the paramagnetic phase is

$$\mathcal{ ilde{M}}=mmm1'$$

The symmetry operations of the group $\tilde{\mathcal{M}}$, following the notation defined in Appendix A, are:-

$$\hat{g}_{1} = E, \qquad \hat{g}_{9} = \Theta E$$

$$\hat{g}_{2} = \hat{C}_{2z}, \qquad \hat{g}_{10} = \hat{\Theta} \hat{C}_{2z}$$

$$\hat{g}_{3} = \hat{C}_{2y}, \qquad \hat{g}_{11} = \hat{\Theta} \hat{C}_{2y}$$

$$\hat{g}_{4} = \hat{C}_{2x}, \qquad \hat{g}_{12} = \hat{\Theta} \hat{C}_{2x}$$

$$\hat{g}_{5} = \hat{I}, \qquad \hat{g}_{13} = \hat{\Theta} \hat{I}$$

$$\hat{g}_{6} = \hat{\sigma}_{z}, \qquad \hat{g}_{14} = \hat{\Theta} \hat{\sigma}_{z}$$

$$\hat{g}_{7} = \hat{\sigma}_{y}, \qquad \hat{g}_{15} = \hat{\Theta} \hat{\sigma}_{y}$$

$$\hat{q}_{8} = \hat{\sigma}_{x}, \qquad \hat{q}_{16} = \hat{\Theta} \hat{\sigma}_{x}$$

The magnetic symmetries of the ordered phases that may occur below T_c may be determined from a knowledge of the irreducible corepresentations (IC's) of the paramagnetic group $\tilde{\mathcal{M}}$. A comprehensive description of the method for determining the IC's of magnetic point groups may be found in Bradley & Cracknell (1972). Starting from the character table of the irreducible representations of the point group $\tilde{G}_0 = mmm$ (Table 7.3), since the matrices constituting the IC's of the paramagnetic group $\tilde{\mathcal{M}}$ are identical to the matrices of the corresponding IR for $\hat{g}_i \in G_0$ and are multiplied by a factor of (± 1) for $\hat{g}_i \in \hat{\Theta}G_0$, then for the one dimensional IR's of Table 7.3 the character table of the irreducible corepresentations of $\tilde{\mathcal{M}}$ follows immediately. It is illustrated in Table 7.4.

Table 7.3: Character table for the irreducible representations of the point group mmm (Bradley & Cracknell, 1972).

IR	Ê	Ĉ22	\hat{C}_{2y}	\hat{C}_{2x}	Î	$\hat{\sigma}_{\pmb{x}}$	$\hat{\sigma}_{y}$	$\hat{\sigma}_{x}$
Γ_1	1	1	1	1	1	1	1	1
Γ_2	1	-1	1	-1	1	-1	1	-1
Γ3	1	1	-1	-1	1	1	-1	-1
Γ_4	1	-1	-1	1	1	-1	-1	1

Table 7.4: Character table for the irreducible corepresentations of the of the magnetic group Imma1' at k=0.

IC	\hat{g}_1	ĝ2	ĝ3	ĝ4	ĝ5	ĝ6	ĝ7	ĝ ₈	ĝ ₉	\hat{g}_{10}	ĝ ₁₁	ĝ12	ĝ13	ĝ14	\hat{g}_{15}	\hat{g}_{16}
$\mathcal{D}\Gamma_1^+$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\mathcal{D}\Gamma_2^+$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
$\mathcal{D}\Gamma_3^+$	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1
$\mathcal{D}\Gamma_4^+$	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1
$\mathcal{D}\Gamma_1^-$	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1
$\mathcal{D}\Gamma_2^-$	1	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1
$\mathcal{D}\Gamma_3^-$	1	1	-1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1
$\mathcal{D}\Gamma_4^-$	1	-1	-1	1	1	-1	-1	1	-1	1	1	-1	-1	1	1	-1

Table 7.5: Symmetry operations of mmm1' (i.e. Imma1' at k=0) leaving invariant the variation of the average density of the magnetic moments.

IC								
$\mathcal{D}\Gamma_1^-$	\hat{g}_1	\hat{g}_2	\hat{g}_{3}	\hat{g}_4	\hat{g}_{5}	\hat{g}_{6}	\hat{g}_{7}	\hat{g}_{8}
$\mathcal{D}\Gamma_2^-$	\hat{g}_1	ĝ3	\hat{g}_{5}	ĝ7	\hat{g}_{10}	\hat{g}_{12}	\hat{g}_{14}	\hat{g}_{16}
$\mathcal{D}\Gamma_3^-$	ĝ1	ĝ2	\hat{g}_{5}	ĝ ₆	\hat{g}_{11}	\hat{g}_{12}	ĝ15	\hat{g}_{16}
$\mathcal{D}\Gamma_4^-$	\hat{g}_1	ĝ4	\hat{g}_5	ĝ8	ĝ10	\hat{g}_{11}	ĝ14	\hat{g}_{15}



Figure 7.3: The possible magnetic ordering in a crystallographic unit cell of CeSi_{x} induced by the irreducible corepresentations $\mathcal{D}\Gamma_{\iota}^{-}$ ($\iota = 1, \ldots, 4$) of the magnetic group mmm1'.

For transitions from a paramagnetic to a magnetically ordered phase only the odd corepresentations $\mathcal{D}\Gamma_{\iota}^{-}$ ($\iota = 1, ..., 4$) in Table 7.4 need to be considered. Recalling equation (5.62), i.e.

$$\mu_i(r) = \sum_{\iota, \alpha} N_{i\alpha}^\iota \phi_\alpha^\iota(r)$$

then for each of the one-dimensional IC's $\mathcal{D}\Gamma_{\iota}^{-}$ there will be only one component α in the expansion of μ that needs to be considered. The variation of the average density of the magnetic moments in the crystal may thus be written as

$$\delta\mu^{\iota} = N^{\iota}\phi^{\iota}$$

where ϕ^{ι} is a basis spanning the ι^{th} IC of the group $\tilde{\mathcal{M}}$ and N^{ι} transforms as the direct product of the ι^{th} IC of the group $\tilde{\mathcal{M}}$ and also of the vectorial representation of this group. It may be seen from Table 7.4 that the symmetry operations of mmml' that leave $\delta \mu^{\iota}$ invariant for each $\mathcal{D}\Gamma_{\iota}^{-}$ are those listed in Table 7.5. Fig. 7.3 illustrates the nature of the ordering expected for each of these groups, assuming the magnetic moments orientate along the z-axis, as defined in Fig. 5.4.

Determination of the basis functions of the CeSi_x unit cell magnetization vectors M, L_β ($\beta = 1, 2, 3$) associated with the IC's of the magnetic point group mmm1'

The basis functions of the CeSi_x unit cell magnetization vectors M, L_β ($\beta = 1, 2, 3$) associated with the irreducible corepresentations of the magnetic point group mmm1'(i.e. associated to the magnetic space group Imma1' at k = 0) may be determined via the use of projection operators, similar to those described in § 5.1. The projection of a vector M onto the space associated with the IC $\mathcal{D}\Gamma_t$ of the magnetic group $\tilde{\mathcal{M}}$ is given by

$$M^{\mathcal{D}\Gamma_{\iota}} = \hat{P}_{\iota}M \tag{7.2}$$

where

$$\hat{P}_{\iota} = \frac{l_{\iota}}{d(\tilde{\mathcal{M}})} \sum_{\hat{\sigma} \in \tilde{\mathcal{M}}} \chi_{\iota}^{*}(\hat{g}) \hat{g}$$
(7.3)

and l_{ι} is the dimensionality of the IC $\mathcal{D}\Gamma_{\iota}$, $d(\tilde{\mathcal{M}})$ is the number of symmetry operations $\hat{g} \in \tilde{\mathcal{M}}$ and $\chi_{\iota}^{*}(\hat{g})$ is the complex conjugate of the character of the symmetry element \hat{g} within the IC $\mathcal{D}\Gamma_{\iota}$. Using the character table for the IC's of the magnetic group mmm1' (Table 7.4), the transformation properties of the vectors M, L_{β} $(\beta = 1, 2, 3)$ under the symmetry operations of the paramagnetic group mmm1' (Table 5.4) and the spatial transformation of the components of a magnetic moment μ under the symmetry operations of the crystallographic point group mmm (Table 5.5), then applying (7.2) and (7.3) we obtain:- Projection onto the vector space of symmetry $\mathcal{D}\Gamma_1^-$

.

$$\begin{split} M_x^{\mathcal{D}\Gamma_1^-} &= \frac{1}{16} \left[1.1.(M_x) + 1.1.(-M_x) + 1.1.(-M_x) + 1.1.(M_x) \\ &+ 1.1.(M_x) + 1.1.(-M_x) + 1.1.(-M_x) + 1.1.(M_x) \\ &+ -1. - 1.(M_x) + -1. - 1.(-M_x) + -1. - 1.(-M_x) + -1. - 1.(M_x) \\ &+ -1. - 1.(M_x) + -1. - 1.(-M_x) + -1. - 1.(-M_x) + -1. - 1.(M_x) \right] \\ &\Rightarrow M_x^{\mathcal{D}\Gamma_1^-} = 0 \end{split}$$

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$$M_{y}^{\mathcal{D}\Gamma_{1}^{-}} = \frac{1}{16} \left[1.1.(M_{y}) + 1.1.(-M_{y}) + 1.1.(M_{y}) + 1.1.(-M_{y}) \right. \\ \left. + 1.1.(M_{y}) + 1.1.(-M_{y}) + 1.1.(M_{y}) + 1.1.(-M_{y}) \right. \\ \left. + -1. - 1.(M_{y}) + -1. - 1.(-M_{y}) + -1. - 1.(M_{y}) + -1. - 1.(-M_{y}) \right. \\ \left. + -1. - 1.(M_{y}) + -1. - 1.(-M_{y}) + -1. - 1.(M_{y}) + -1. - 1.(-M_{y}) \right] \\ \left. \Rightarrow M_{y}^{\mathcal{D}\Gamma_{1}^{-}} = 0 \right]$$

$$\begin{split} M_z^{\mathcal{D}\Gamma_1^-} &= \frac{1}{16} \left[1.1.(M_z) + 1.1.(M_z) + 1.1.(-M_z) + 1.1.(-M_z) \right. \\ &\quad + 1.1.(M_z) + 1.1.(M_z) + 1.1.(-M_z) + 1.1.(-M_z) \\ &\quad + -1. - 1.(M_z) + -1. - 1.(M_z) + -1. - 1.(-M_z) + -1. - 1.(-M_z) \\ &\quad + -1. - 1.(M_z) + -1. - 1.(M_z) + -1. - 1.(-M_z) + -1. - 1.(-M_z) \right] \\ &\qquad \Rightarrow M_z^{\mathcal{D}\Gamma_1^-} = 0 \end{split}$$

Since L_3 has the same transformation properties as M then

$$L_{3x}^{\mathcal{D}\Gamma_1^-} = L_{3y}^{\mathcal{D}\Gamma_1^-} = L_{3z}^{\mathcal{D}\Gamma_1^-} = 0$$

$$L_{1x}^{\mathcal{D}\Gamma_{1}^{-}} = \frac{1}{16} \left[1.1.(L_{1x}) + 1.1.(-L_{1x}) + 1. - 1.(-L_{1x}) + 1. - 1.(L_{1x}) + 1. - 1.(L_{1x}) + 1. - 1.(-L_{1x}) + 1.1.(-L_{1x}) + 1.1.(L_{1x}) + 1. - 1.(-L_{1x}) + 1.1.(-L_{1x}) + - 1. - 1.(-L_{1x}) + - 1. - 1.(-L_{1x}) \right]$$

$$\Rightarrow L_{1x}^{\mathcal{D}\Gamma_{1}^{-}} = 0$$

$$L_{1y}^{\mathcal{D}\Gamma_{1}^{-}} = \frac{1}{16} [1.1.(L_{1y}) + 1.1.(-L_{1y}) + 1. - 1.(L_{1y}) + 1. - 1.(-L_{1y}) \\ + 1. - 1.(L_{1y}) + 1. - 1.(-L_{1y}) + 1.1.(L_{1y}) + 1.1.(-L_{1y}) \\ + - 1. - 1.(L_{1y}) + -1. - 1.(-L_{1y}) + -1.1.(L_{1y}) + -1.1.(-L_{1y}) \\ + - 1.1.(L_{1y}) + -1.1.(-L_{1y}) + -1. - 1.(L_{1y}) + -1. - 1.(-L_{1y})] \\ \Rightarrow L_{1y}^{\mathcal{D}\Gamma_{1}^{-}} = 0$$

$$L_{1z}^{\mathcal{D}\Gamma_{1}^{-}} = \frac{1}{16} \left[1.1.(L_{1z}) + 1.1.(L_{1z}) + 1. - 1.(-L_{1z}) + 1. - 1.(-L_{1z}) + 1. - 1.(L_{1z}) + 1. - 1.(L_{1z}) + 1.1.(-L_{1z}) + 1.1.(-L_{1z}) + 1.1.(-L_{1z}) + -1. - 1.(L_{1z}) + -1. - 1.(L_{1z}) + -1.1.(-L_{1z}) + -1.1.(-L_{1z}) + -1.1.(-L_{1z}) + -1.1.(-L_{1z}) + -1.1.(-L_{1z}) + -1. - 1.(-L_{1z}) \right]$$

$$\Rightarrow L_{1z}^{\mathcal{D}\Gamma_{1}^{-}} = 0$$

Since L_2 has the same transformation properties as L_1 then

$$L_{2x}^{\mathcal{D}\Gamma_{1}^{-}} = L_{2y}^{\mathcal{D}\Gamma_{1}^{-}} = L_{2z}^{\mathcal{D}\Gamma_{1}^{-}} = 0$$

Projection onto the vector space of symmetry $\mathcal{D}\Gamma_2^-$

$$M_x^{\mathcal{P}\Gamma_2^-} = \frac{1}{16} \left[1.1.(M_x) + -1.1.(-M_x) + 1.1.(-M_x) + -1.1.(M_x) + 1.1.(-M_x) + -1.1.(M_x) + 1.1.(-M_x) + 1.1.(-M_x) + -1.1.(-M_x) + -1.1.(-M_x) + 1.-1.(-M_x) \right]$$

$$\Rightarrow M_x^{\mathcal{P}\Gamma_2^-} = 0$$

$$\begin{split} M_y^{\mathcal{D}\Gamma_2^-} &= \frac{1}{16} \left[1.1.(M_y) + -1.1.(-M_y) + 1.1.(M_y) + -1.1.(-M_y) \right. \\ &\quad + 1.1.(M_y) + -1.1.(-M_y) + 1.1.(M_y) + -1.1.(-M_y) \\ &\quad + -1. - 1.(M_y) + 1. - 1.(-M_y) + -1. - 1.(M_y) + 1. - 1.(-M_y) \\ &\quad + -1. - 1.(M_y) + 1. - 1.(-M_y) + -1. - 1.(M_y) + 1. - 1.(-M_y) \right] \\ &\qquad \Rightarrow M_y^{\mathcal{D}\Gamma_2^-} = M_y \end{split}$$

$$\begin{split} M_z^{\mathcal{D}\Gamma_2^-} &= \frac{1}{16} \left[1.1.(M_z) + -1.1.(M_z) + 1.1.(-M_z) + -1.1.(-M_z) \right. \\ &\quad + 1.1.(M_z) + -1.1.(M_z) + 1.1.(-M_z) + -1.1.(-M_z) \\ &\quad + -1. - 1.(M_z) + 1. - 1.(M_z) + -1. - 1.(-M_z) + 1. - 1.(-M_z) \right. \\ &\quad + -1. - 1.(M_z) + 1. - 1.(M_z) + -1. - 1.(-M_z) + 1. - 1.(-M_z) \right] \\ &\qquad \Rightarrow M_z^{\mathcal{D}\Gamma_2^-} = 0 \end{split}$$

Since L_3 has the same transformation properties as M then

.

$$L_{3x}^{\mathcal{D}\Gamma_{2}^{-}} = L_{3z}^{\mathcal{D}\Gamma_{2}^{-}} = 0$$
 and $L_{3y}^{\mathcal{D}\Gamma_{2}^{-}} = L_{3y}$

$$L_{1x}^{\mathcal{D}\Gamma_{2}^{-}} = \frac{1}{16} \left[1.1.(L_{1x}) + -1.1.(-L_{1x}) + 1. - 1.(-L_{1x}) + -1. - 1.(L_{1x}) + 1. - 1.(L_{1x}) + -1. - 1.(-L_{1x}) + 1.1.(-L_{1x}) + -1.1.(L_{1x}) + -1. - 1.(-L_{1x}) + 1. - 1.(-L_{1x}) + -1.1.(-L_{1x}) + 1. - 1.(-L_{1x}) + 1. - 1$$

$$\Rightarrow L_{1x}^{\mathcal{D}\Gamma_2^-} = 0$$

$$L_{1y}^{\mathcal{D}\Gamma_{2}^{-}} = \frac{1}{16} \left[1.1.(L_{1y}) + -1.1.(-L_{1y}) + 1. - 1.(L_{1y}) + -1. - 1.(-L_{1y}) \right. \\ \left. + 1. - 1.(L_{1y}) + -1. - 1.(-L_{1y}) + 1.1.(L_{1y}) + -1.1.(-L_{1y}) \right. \\ \left. + -1. - 1.(L_{1y}) + 1. - 1.(-L_{1y}) + -1.1.(L_{1y}) + 1.1.(-L_{1y}) \right. \\ \left. + -1.1.(L_{1y}) + 1.1.(-L_{1y}) + -1. - 1.(L_{1y}) + 1. - 1.(-L_{1y}) \right] \\ \left. \Rightarrow L_{1y}^{\mathcal{D}\Gamma_{2}^{-}} = 0 \right]$$

$$\begin{split} L_{1z}^{\mathcal{D}\Gamma_{2}^{-}} &= \frac{1}{16} \left[1.1.(L_{1z}) + -1.1.(L_{1z}) + 1. - 1.(-L_{1z}) + -1. - 1.(-L_{1z}) \right. \\ &+ 1. - 1.(L_{1z}) + -1. - 1.(L_{1z}) + 1.1.(-L_{1z}) + -1.1.(-L_{1z}) \\ &+ -1. - 1.(L_{1z}) + 1. - 1.(L_{1z}) + -1.1.(-L_{1z}) + 1.1.(-L_{1z}) \\ &+ -1.1.(L_{1z}) + 1.1.(L_{1z}) + -1. - 1.(-L_{1z}) + 1. - 1.(-L_{1z}) \right] \\ &\Rightarrow L_{1z}^{\mathcal{D}\Gamma_{2}^{-}} = 0 \end{split}$$

Since L_2 has the same transformation properties as L_1 then

$$L_{2x}^{\mathcal{D}\Gamma_{2}^{-}} = L_{2y}^{\mathcal{D}\Gamma_{2}^{-}} = L_{2z}^{\mathcal{D}\Gamma_{2}^{-}} = 0$$

Projection onto the vector space of symmetry $\mathcal{D}\Gamma_3^-$

$$M_x^{\mathcal{D}\Gamma_s^-} = \frac{1}{16} [1.1.(M_x) + 1.1.(-M_x) + -1.1.(-M_x) + -1.1.(M_x) \\ + 1.1.(M_x) + 1.1.(-M_x) + -1.1.(-M_x) + -1.1.(M_x) \\ + -1. - 1.(M_x) + -1. - 1.(-M_x) + 1. - 1.(-M_x) + 1. - 1.(M_x) \\ + -1. - 1.(M_x) + -1. - 1.(-M_x) + 1. - 1.(-M_x) + 1. - 1.(M_x)] \\ \Rightarrow M_x^{\mathcal{D}\Gamma_s^-} = 0$$

$$M_{y}^{\mathcal{P}\Gamma_{s}^{-}} = \frac{1}{16} [1.1.(M_{y}) + 1.1.(-M_{y}) + -1.1.(M_{y}) + -1.1.(-M_{y}) \\ + 1.1.(M_{y}) + 1.1.(-M_{y}) + -1.1.(M_{y}) + -1.1.(-M_{y}) \\ + -1. - 1.(M_{y}) + -1. - 1.(-M_{y}) + 1. - 1.(M_{y}) + 1. - 1.(-M_{y}) \\ + -1. - 1.(M_{y}) + -1. - 1.(-M_{y}) + 1. - 1.(M_{y}) + 1. - 1.(-M_{y})] \\ \Rightarrow M_{y}^{\mathcal{P}\Gamma_{s}^{-}} = 0$$

$$M_{z}^{\mathcal{D}\Gamma_{s}^{-}} = \frac{1}{16} \left[1.1.(M_{z}) + 1.1.(M_{z}) + -1.1.(-M_{z}) + -1.1.(-M_{z}) \right. \\ \left. + 1.1.(M_{z}) + 1.1.(M_{z}) + -1.1.(-M_{z}) + -1.1.(-M_{z}) \right. \\ \left. + -1. - 1.(M_{z}) + -1. - 1.(M_{z}) + 1. - 1.(-M_{z}) + 1. - 1.(-M_{z}) \right. \\ \left. + -1. - 1.(M_{z}) + -1. - 1.(M_{z}) + 1. - 1.(-M_{z}) + 1. - 1.(-M_{z}) \right] \\ \left. \Rightarrow M_{z}^{\mathcal{D}\Gamma_{s}^{-}} = M_{z} \right]$$

Since L_3 has the same transformation properties as M then

$$L_{3x}^{\mathcal{D}\Gamma_{3}^{-}} = L_{3y}^{\mathcal{D}\Gamma_{3}^{-}} = 0 \qquad \text{and} \qquad L_{3z}^{\mathcal{D}\Gamma_{3}^{-}} = L_{3z}$$

$$L_{1x}^{\mathcal{D}\Gamma_{3}^{-}} = \frac{1}{16} \left[1.1.(L_{1x}) + 1.1.(-L_{1x}) + -1. - 1.(-L_{1x}) + -1. - 1.(L_{1x}) + 1. - 1.(L_{1x}) + 1. - 1.(-L_{1x}) + -1.1.(-L_{1x}) + -1.1.(L_{1x}) + -1. - 1.(-L_{1x}) + -1.1.(-L_{1x}) + 1.1.(-L_{1x}) + 1.1.(-L_{1x}) + 1.1.(-L_{1x}) + 1.1.(-L_{1x}) + 1.1.(-L_{1x}) + 1. - 1.(-L_{1x}) + 1. - 1.(-L_{1x}) + 1. - 1.(-L_{1x}) \right]$$

$$\Rightarrow L_{1x}^{\mathcal{D}\Gamma_{\mathbf{3}}^{-}} = 0$$

$$L_{1y}^{\mathcal{P}\Gamma_{3}^{-}} = \frac{1}{16} \left[1.1.(L_{1y}) + 1.1.(-L_{1y}) + -1. - 1.(L_{1y}) + -1. - 1.(-L_{1y}) \right. \\ \left. + 1. - 1.(L_{1y}) + 1. - 1.(-L_{1y}) + -1.1.(L_{1y}) + -1.1.(-L_{1y}) \right. \\ \left. + - 1. - 1.(L_{1y}) + -1. - 1.(-L_{1y}) + 1.1.(L_{1y}) + 1.1.(-L_{1y}) \right. \\ \left. + - 1.1.(L_{1y}) + -1.1.(-L_{1y}) + 1. - 1.(L_{1y}) + 1. - 1.(-L_{1y}) \right] \\ \Rightarrow L_{1y}^{\mathcal{P}\Gamma_{3}^{-}} = 0$$

$$L_{1z}^{D\Gamma_{3}^{-}} = \frac{1}{16} \left[1.1.(L_{1z}) + 1.1.(L_{1z}) + -1. - 1.(-L_{1z}) + -1. - 1.(-L_{1z}) + 1. - 1.(L_{1z}) + 1. - 1.(L_{1z}) + -1.1.(-L_{1z}) + 1. - 1.(L_{1z}) + 1. - 1.(L_{1z}) + -1. - 1.(L_{1z}) + 1.1.(-L_{1z}) + 1. - 1.(-L_{1z}) + 1. - 1.(-L_{1z}) + 1. - 1.(-L_{1z}) + 1. - 1.(-L_{1z}) \right]$$
$$\Rightarrow L_{1z}^{D\Gamma_{3}^{-}} = 0$$

Since L_2 has the same transformation properties as L_1 then

$$L_{2x}^{\mathcal{D}\Gamma_{3}^{-}} = L_{2y}^{\mathcal{D}\Gamma_{3}^{-}} = L_{2z}^{\mathcal{D}\Gamma_{3}^{-}} = 0$$

Projection onto the vector space of symmetry $\mathcal{D}\Gamma_4^-$

$$M_x^{\mathcal{D}\Gamma_4^-} = \frac{1}{16} \left[1.1.(M_x) + -1.1.(-M_x) + -1.1.(-M_x) + 1.1.(M_x) + 1.1.(M_x) + -1.1.(-M_x) + -1.1.(-M_x) + 1.1.(M_x) + -1.-1.(M_x) + 1. - 1.(-M_x) + 1. - 1.(-M_x) + -1. - 1.(M_x) + -1. - 1.(M_x) + 1. - 1.(-M_x) + 1. - 1.(-M_x) + -1. - 1.(M_x) \right]$$

$$\Rightarrow M_x^{\mathcal{D}\Gamma_4^-} = M_x$$

$$M_{y}^{\mathcal{D}\Gamma_{4}^{-}} = \frac{1}{16} [1.1.(M_{y}) + -1.1.(-M_{y}) + -1.1.(M_{y}) + 1.1.(-M_{y}) \\ + 1.1.(M_{y}) + -1.1.(-M_{y}) + -1.1.(M_{y}) + 1.1.(-M_{y}) \\ + -1. - 1.(M_{y}) + 1. - 1.(-M_{y}) + 1. - 1.(M_{y}) + -1. - 1.(-M_{y}) \\ + -1. - 1.(M_{y}) + 1. - 1.(-M_{y}) + 1. - 1.(M_{y}) + -1. - 1.(-M_{y})] \\ \Rightarrow M_{y}^{\mathcal{D}\Gamma_{4}^{-}} = 0$$

$$M_{z}^{\mathcal{D}\Gamma_{4}^{-}} = \frac{1}{16} \left[1.1.(M_{z}) + -1.1.(M_{z}) + -1.1.(-M_{z}) + 1.1.(-M_{z}) \right. \\ \left. + 1.1.(M_{z}) + -1.1.(M_{z}) + -1.1.(-M_{z}) + 1.1.(-M_{z}) \right. \\ \left. + -1. - 1.(M_{z}) + 1. - 1.(M_{z}) + 1. - 1.(-M_{z}) + -1. - 1.(-M_{z}) \right. \\ \left. + -1. - 1.(M_{z}) + 1. - 1.(M_{z}) + 1. - 1.(-M_{z}) + -1. - 1.(-M_{z}) \right] \\ \left. \Rightarrow M_{z}^{\mathcal{D}\Gamma_{4}^{-}} = 0 \right]$$

Since L_3 has the same transformation properties as M then

•

$$L_{3y}^{\mathcal{D}\Gamma_{4}^{-}} = L_{3z}^{\mathcal{D}\Gamma_{4}^{-}} = 0$$
 and $L_{3x}^{\mathcal{D}\Gamma_{4}^{-}} = L_{3x}$

$$L_{1x}^{\mathcal{D}\Gamma_{4}^{-}} = \frac{1}{16} \left[1.1.(L_{1x}) + -1.1.(-L_{1x}) + -1. - 1.(-L_{1x}) + 1. - 1.(L_{1x}) + 1. - 1.(L_{1x}) + -1. - 1.(-L_{1x}) + -1.1.(-L_{1x}) + 1.1.(L_{1x}) + -1. - 1.(L_{1x}) + 1. - 1.(-L_{1x}) + 1.1.(-L_{1x}) + -1.1.(L_{1x}) + -1.1.(L_{1x}) + 1.1.(-L_{1x}) + 1. - 1.(-L_{1x}) + 1. - 1.(-L_{1x}) + -1. - 1.(L_{1x}) \right]$$

$$\Rightarrow L_{1x}^{\mathcal{D}\Gamma_4} = 0$$

$$L_{1y}^{\mathcal{D}\Gamma_{4}^{-}} = \frac{1}{16} \left[1.1.(L_{1y}) + -1.1.(-L_{1y}) + -1. - 1.(L_{1y}) + 1. - 1.(-L_{1y}) + 1. - 1.(L_{1y}) + -1. - 1.(-L_{1y}) + -1.1.(-L_{1y}) + 1. - 1.(-L_{1y}) + -1.1.(-L_{1y}) + -1.1.(-L_{1y}) + 1. - 1.(-L_{1y}) + 1. - 1.(-L_{1y}) + 1. - 1.(-L_{1y}) + 1. - 1.(-L_{1y}) \right]$$

$$\Rightarrow L_{1y}^{\mathcal{D}\Gamma_{4}^{-}} = 0$$

$$\begin{split} L_{1z}^{\mathcal{D}\Gamma_{4}^{-}} &= \frac{1}{16} \left[1.1.(L_{1z}) + -1.1.(L_{1z}) + -1. - 1.(-L_{1z}) + 1. - 1.(-L_{1z}) \right. \\ &+ 1. - 1.(L_{1z}) + -1. - 1.(L_{1z}) + -1.1.(-L_{1z}) + 1.1.(-L_{1z}) \\ &+ -1. - 1.(L_{1z}) + 1. - 1.(L_{1z}) + 1.1.(-L_{1z}) + -1.1.(-L_{1z}) \\ &+ -1.1.(L_{1z}) + 1.1.(L_{1z}) + 1. - 1.(-L_{1z}) + -1. - 1.(-L_{1z}) \right] \\ &\Rightarrow L_{1z}^{\mathcal{D}\Gamma_{4}^{-}} = 0 \end{split}$$

Since L_2 has the same transformation properties as L_1 then

$$L_{2x}^{\mathcal{D}\Gamma_{4}^{-}} = L_{2y}^{\mathcal{D}\Gamma_{4}^{-}} = L_{2z}^{\mathcal{D}\Gamma_{4}^{-}} = 0$$

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Publications

Journal of Magnetism and Magnetic Materials 104–107 (1992) 657–658 North-Holland



Crystallographic structure and magnetic ground state of CeSi,

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The intermetallic compound CeSi_x (x = 1.80, 1.85) has been investigated by neutron powder diffraction using the diffractometer D2B at the ILL, Grenoble. For both samples the coexistence of two structural phases was observed. In the case of $\text{CeSi}_{1.85}$, these two phases are of the same spacegroup but with a different temperature variation of their lattice parameters. A dependence of the magnetic ground state of $\text{CeSi}_{1.80}$ on the heat treatment of the sample was also observed. The importance of the ordering of holes in the Si lattice of CeSi_2 in determining the ground state properties of CeSi_x is discussed.

The binary intermetallic compound CeSi_x with x in the range 1.6-2.0 crystallizes in either the α -ThSi₂ structure for x > 1.80 or the α -GdSi₂ structure for lower Si concentrations. The crystallographic properties of rate-earth disilicides have been investigated extensively [1]. Here we report on a detailed investigation of two CeSi_x samples with composition x = 1.80and 1.85 by neutron powder diffraction.

The samples were prepared by melting high-purity constituents together in the appropriate ratios using an argon arc furnace. Each sample was remelted at least five times to ensure a homogeneous mixture. Weight losses in all cases were less than 1%. After the sample preparation the ingots were crushed and passed through a 250 μ m sieve. The powder was then sealed under vacuum in a quartz tube and heat treated at a temperature of 900 °C for 48 h. Finally, following the heat treatment, the samples were quenched into ice water.

Neutron powder diffraction experiments were carried out using the diffractometer D2B at the high flux reactor at the ILL in Grenoble, France. Diffraction patterns were recorded over the temperature range 1.5 to 300 K at intervals of 50 K. Each diffraction pattern was refined using a multiphase profile refinement program [2]. For the CeSi_{1.85} compound it was necessary to refine the powder diffraction pattern using two structural phases of the same spacegroup. Over the entire temperature range investigated here, peak splitting of certain high angle reflections was observed for both CeSi_{1.80} and CeSi_{1.85}, confirming the existence of two structural phases. For the CeSi_{1.80} compound, an investigation is currently carried out to determine whether the small peak splitting observed is to be attributed to a second α -GdSi₂ structure or to a lower symmetry Imma spacegroup.

The variation of the lattice parameters of $\text{CeSi}_{1.85}$ over the whole temperature range from 1.5 to 300 K is shown in fig. 1. The difference between the lattice parameters for the two phases is small and therefore the observation of a separation of Bragg peaks in the diffraction pattern requires a high resolution and the investigation of large values of 2θ . The evidence for



Fig. 1. Variation of the lattice parameters with temperature for the two 14_1 /amd phases of $\text{CeSi}_{1.85}$. Refinements consistently gave one Si-"rich" phase ($x \approx 2$) and one Si-"poor" phase ($x \approx 1.8$). However, for the high-temperature data (T >250 K), where the observed peak splitting is small, there is some ambiguity as to which phase is Si-"rich" or -"poor". Within the uncertainty of the refinement the data points above 250 K may be inverted.

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the coexistence of two structural phases has been reported by other research groups [1,3] for samples with various compositions and prepared by different methods. In all cases a two phase sample is observed for $CeSi_{1.85}$.

The magnetic properties of the samples were characterised by susceptibility measurements [4]. The CeSi_{1.85} samples were observed to be paramagnetic down to 1.5 K, the lowest temperature investigated in these experiments. However for CeSi_{1.80} samples, depending on their heat treatment, a ferromagnetic ($T_c \approx$ 12 K) or paramagnetic state (at 1.5 K) was observed. This result is interpreted in terms of ordering of the holes in the Si sublattice of CeSi₂. The hole ordering of the Si sublattice is believed to be important for the occurance of ferromagnetic order at low temperatures.

Similar investigations concerning the crystallographic characteristics of CeSi, have been carried out by Dijkman et al. [5] and also by Koghi et al. [3]. While the coexistence of two structural phase is also observed in their experiments, Koghi et al. have interpreted their neutron diffraction patterns in terms of a temperature-dependent ratio of the two phases. Our investigations indicate a fixed ratio of the two phases with the coexistence extending to at least 300 K. In another investigation by neutron powder diffraction by Madar et al. [1], a temperature dependence of the relative proportion of the phases was assumed and it was concluded that the two structural phases did not coexist beyond 280 K. However, it must be noted that their conclusions were based on results obtained only for 2θ values up to 100°, therefore not making full use of the high resolution available on D2B. For temperatures above 250 K the difference between the lattice parameters for the two phases is so small that peak splitting is only observed at higher scattering angles than those investigated by Madar et al. [1].

An interesting aspect of the present investigation is the occurance or absence of ferromagnetism at low temperatures in $\text{CeSi}_{1.80}$ depending on the heat treatment of the sample. It was suggested by Madar et al. [1] that it is the ordering of Si vacancies which is the important mechanism for the formation of the various phases in CeSi_x compounds. The observation of differing ground states for samples with identical chemical composition but different heat treatment of the sample supports this interpretation. The heat treatment is expected to influence the ordering of holes on the Si sublattice but it will not affect the chemical order of Ce or Si atoms. It is therefore argued that it is not the electron concentration which is the important parameter for the occurance of absence of ferromagnetic order but rather the arrangement of holes, the ordering of which is determined by heat treatment. A thermodynamic model has been put forward for CeSi_x by Murashita et al. [6] and applied to the variation of the e-axis with composition. However, for a more realistic model the possibility of order and disorder of holes on the Si sublattice has to be included. The authors are presently pursuing an extension of a thermodynamic model along these lines.

Despite the fact that rare-earth disilicides have been worked upon for more than twenty years, these compounds still provide a large variety of physical phenomena which are as yet not fully understood. In particular, the interpretation of CeSi_x compounds as dense ferromagnetic Kondo systems requires an understanding of the factors influencing the formation of a ferromagnetic ground state. The observation of phase transitions or phase separations and the importance of the ordering of the holes on the Si lattice suggests that additional degrees of freedom, such as that of the lattice, are of importance in determining the ground state properties.

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Physica B 180 & 181 (1992) 601-602 North-Holland



Investigation of the crystallographic properties of CeSi_x and their relation to a magnetically ordered ground state

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The intermetallic compound $CcSi_x$ (x = 1.80, 1.85) has been investigated by neutron powder diffraction using the diffractometer D2B at the ILL, Grenoble. The coexistence of two structural phases was observed for both samples; for $CeSi_{1.85}$ the two phases are of the same spacegroup but with a different temperature variation of their lattice parameters. A dependence of the magnetic ground state of $CeSi_{1.80}$ on the heat treatment of the sample was also observed. A simple thermodynamic model is presented which can qualitatively account for the two phase structures of these samples and indicates an ordering of vacancies on the Si lattice sites of one phase. The importance of such an ordering of holes in determining the ground state properties of CeSi, is discussed.

1. Introduction

The binary intermetallic compound CeSi_x with x in the range 1.6 - > 2.0 crystallizes in either the ThSi_2 structure for x > 1.80 or the GdSi_2 structure for lower Si concentrations. The crystallographic properties of rare-earth disilicides have been investigated extensively [1]. We present here the results of a detailed investigation of two CeSi_x samples, $\text{CeSi}_{1.80}$ and $\text{CeSi}_{1.85}$, by neutron powder diffraction.

2. Experimental

The samples were prepared by melting high purity constituents together in an Argon Arc furnace. Each sample was remelted at least five times to ensure a homogeneous mixture. Weight losses in all cases were less than 1%. After the sample preparation the ingots were crushed and passed through a 250 μ m sieve. The powder was then sealed under vacuum in a quartz tube and heat treated at a temperature of 900°C for 48 hours. Finally, following the heat treatment, the samples were quenched into ice water.

Neutron powder diffraction experiments were carried out using the diffractometer D2B at the high flux reactor at the ILL in Grenoble, France. Diffraction patterns were recorded over the temperature range 1.5-300 K at intervals of 50 K. Each diffraction pattern was refined using a multiphase profile refinement program [2]. For the CeSi_{1.85} compound it was necessary to refine the powder diffraction pattern using two structural phases of the same spacegroup. Over the entire temperature range investigated here, peak splitting of certain high angle reflections were observed for both CeSi_{1.80} and CeSi_{1.85}, confirming the existence of two structural phases. For the CeSi_{1.80} compound, an investigation is currently being carried out to determine whether the two phases have the same spacegroup, that of the GdSi₂ structure, or if the second phase is to be attributed to a lower symmetry Imma spacegroup.

The evidence for the coexistence of two structural phases has been reported by other research groups [1, 3] for samples with various compositions and prepared by different methods. In all cases a two phase sample is observed for the nominal composition of $CeSi_{1.85}$.

The magnetic properties of the samples were characterized by susceptibility measurements. The CeSi_{1.85} samples were observed to be paramagnetic down to 1.5 K, the lowest temperature investigated in these experiments. However for the CeSi_{1.80} samples, depending on their heat treatment, a ferromagnetic $(T_c \approx 12 \text{ K})$ or a paramagnetic state (at 1.5 K) was observed. This result is interpreted in terms of ordering of the holes in the Si sublattice of CeSi₂. Such a hole ordering is believed to be important for the occurrence of ferromagnetic order at low temperatures.

3. Discussion

It has been suggested by Madar et al. [1] that it is the ordering of Si vacancies which is the important mechanism for the formation of the various phases in CeSi_x compounds. The observation of differing ground state for samples with identical chemical composition but prepared by different heat treatments supports this interpretation.

The dynamics of the holes in CeSi_x samples can be understood on the basis of a simple thermodynamic model. A phase separation into a Si rich and a Si poor phase is obtained if it is assumed that the free energy, F, is a convex function of the hole concentration, x. Let F(x) be the free energy of a hole concentration given by x, then for some difference in hole concen-

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Fig. 1. Helmholtz Free Energy, F, as a function of hole concentration, x. $2F(x_1) > F(x_0) + F(x_2) = F(x_1 - \Delta x) + F(x_1 + \Delta x)$.

tration, Δx , the sum of the free energies $F(x + \Delta x)$ and $F(x - \Delta x)$ is smaller than 2F(x), (see fig. 1). Thus taking Δx as a variational parameter, this results in the free energy of two phases with different hole concentrations having a lower free energy compared to a phase in which the distribution of holes is homogeneous.

Now consider the phase with the larger concentration of holes. It is assumed to be described by a CeSi₂ structure with all holes evenly distributed over all available Si sites. This will maximize the entropy Sand thus minimize the free energy, F = E - TS, rendering this arrangement to be stable at higher temperatures. At low temperatures it is the energy E which has to be minimized in order to obtain a minimum of F. This can be achieved by the following mechanism: the lattice is slightly distorted $(ThSi_2 \rightarrow GdSi_2 \text{ structure type})$ making the *a* and *b* axes different and splitting up the Si lattice sites into two inequivalent groups. Thus the energy of the two Si sites will also be different. The total energy can be

minimized by allowing the holes to preferentially occupy Si sites which have the higher energy, resulting in an overall reduction of F for the distorted structure with hole ordering on one of the Si sites compared to a homogeneous CeSi, structure.

A more detailed analysis requires a knowledge of the thermodynamic functions. However, it is encouraging to find experimental evidence for the hole dynamics by the observation of different ground states in $\text{CeSi}_{1.80}$ samples prepared with different heat treatments.

4. Conclusion

The properties of the rare-earth disilicides provide a large variety of physical phenomena which are still as yet not fully understood. In particular, the interpretation of $CeSi_x$ compounds as dense ferromagnetic Kondo systems requires an understanding of the factors influencing the formation of a ferromagnetic ground state. The observation of phase separations or phase transitions and the importance of the ordering of the holes on the Si lattice suggests that additional degrees of freedom, such as that of the lattice, are of importance in determining the ground state properties of $CeSi_x$.

Acknowledgement

The authors would like to express their thanks to R.K. Kremer and M. Babateen for kindly performing the susceptibility measurements on these samples.

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