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**Normal incidence standing wave analysis of the Cu(111)-($\sqrt{3}\times\sqrt{3}$)R30°Mn
structure: Evidence for stacking faults or large scale alloying?**

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Abstract

The interaction of Mn with the Cu(111) surface has been investigated using the normal incidence X-ray standing wave (NIXSW) method. Analysis of the NIXSW was complicated by the apparent large shift in position of many layers of the Cu atoms relative to their expected bulk positions indicated by a change in the coherent position. Quantitative analysis of the NIXSW shows that there are at least two but possibly many sites for each element in the altered layer.

Keywords

X-ray standing wave, copper, manganese.

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Introduction

The widespread interest in the structures formed by Mn on Cu surfaces results from the possibilities of engineering metastable phases with unusual magnetic properties, as the moment carried by Mn atoms is strongly sensitive to local environment. The adsorption of Mn on Cu(100) has been extensively studied. It forms a $c(2\times 2)$ substitutional alloy at around 0.5 ML coverage, with the Mn atoms being proud of the surface by 0.37 ± 0.06 Å [1]. Studies of the interaction of Mn with Cu(111) have been relatively few and far between. An early LEED investigation [2] of Mn on Cu(111) reported an *incommensurate* six-fold symmetric $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure. The authors of this work interpreted this structure by relation to a similar but more deeply studied system, namely a Mn structure on Pd(111) surface [3] formed at elevated temperatures. The incommensurate $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure had an in-plane misfit of $+6.3\pm 1\%$ (equivalent to lattice constant 4.69 Å, giving a nearest neighbour spacing of 2.71 Å). A concurrent series of Auger electron spectroscopy (AES) measurements revealed that the structure involved island growth, rather than a simple single layer.

The determination of the structure of this incommensurate $(\sqrt{3}\times\sqrt{3})R30^\circ$ has not proved easily tractable. A more recent scanning tunnelling microscopy (STM) investigation [4] of Mn on Cu(111) has revealed an interesting complexity in the sub-monolayer coverages grown near room temperature (320 K). The room temperature system shows Stransky-Krastanov growth, that is initially flat but that leads to three-dimensional growth. Further evidence for this growth mode is given by work function measurements that have a shoulder at 1 ML. The STM work reported a lattice constant of 4.89 Å (equivalent to a nearest neighbour spacing of 2.80 Å) and a $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure evident in the STM images. Whereas the more open (100) surface of copper enables Mn atoms to be incorporated, on (111) this only happens at steps. Increased deposition forms compact alloy islands of at least two layers of Cu/Mn.

NIXSW is well established for site determination of adsorbates on metal and semiconductor surfaces. When the X-ray energy is tuned to a Bragg reflection condition the incident and reflected waves interfere to give an X-ray standing wave with a spatial periodicity equal to that of the atomic planes. Scanning the photon energy through this Bragg condition varies the spatial phase of this standing wave, and the measurement of the absorption profile of any atom enables determination of the position of that atom relative to the atomic planes of the substrate. For the study of metals, the influence of mosaicity means that the method can only be applied usefully at normal incidence to a set of atomic planes. Using the [111] and [-111] reflections of a (111) oriented crystal enables a simple geometrical triangulation of the adsorption site, by determination of the atomic position relative to the two sets of atomic planes.

Since it is a method that enables the determination of sites and positions utilising just two measurements and with what is effectively direct data analysis, NIXSW would seem to be an appropriate method for the solution of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure, particularly if the Mn atoms are in a top layer substitution site similar to that found in the $(\sqrt{2}\times\sqrt{2})R45^\circ$ structure found on Cu(100). However, as shown in this paper the measurements reveal that determination of the complete structure is seriously complicated by disturbance of the atomic positions of the Cu species in the substrate. This effect may be interpreted, as is discussed, as evidence either of the formation of a true surface alloy, or of the introduction of stacking faults into the substrate caused by the presence of the Mn species. It should be noted that throughout this work we have not observed an incommensurate $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure, but one that appears to be commensurate with the subsurface lattice.

Experimental details

The NIXSW measurements were made on station 6.3 [5] on the Synchrotron Radiation Source, a station dedicated to NIXSW and SEXAFS measurements. The double-crystal Ge(111) monochromator delivered X-rays at the energy of the Cu(111) Bragg reflection (2965 eV at room temperature) and X-ray absorption was monitored by electron spectroscopy using a concentric hemispherical analyser (CHA). The chamber pressure remained below 1×10^{-9} mbar throughout the experiment.

Mn was deposited in situ from a well-outgassed K-cell and at room temperature. Dose calibration was made by determining the dose required to form a sharp $c(2 \times 2)$ LEED pattern on a separate Cu(100) crystal. The deposition proceeded in instalments in a manner similar to that reported for Mn on Pd(111) [3] but with brief periods of heating to 300°C between approximately 0.1 ML depositions. Around 1 ML was required to form an apparent *commensurate* $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure, the LEED pattern for which is shown in Figure 1. At no time was a room temperature $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure observed (either commensurate or incommensurate).

NIXSW measurements were made from the $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure using both the surface-normal [111] reflection and the [-111] at 70.2° off surface-normal. The X-ray absorption was monitored using 2p_{3/2} photoemission for both Cu and Mn. For each photon energy, the electron emission intensities were determined by recording the difference in number of counts per second on the peak, and the background counts off the peak at a slightly higher electron energy.

Results and discussion

The experimental NIXSW profiles for the $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure are shown in Figure 2 as the data points. The most startling thing about the scans is the data from the [111] reflection monitored using Cu emission. Rather than showing an appropriate substrate reflection curve (shown as a broken line) the shape is changed, which indicates that the top layers of the Cu(111) crystal do not coincide with expected Cu lattice sites. This result would be unexpected for either a simple overlayer of Mn or for a substitutional alloy involving only the top one or two layers. The decay length of Cu $2p_{3/2}$ electrons at this photon energy and take-off angle (35°) is around 8 atomic layers. The disruption to the Cu lattice is to a depth at least comparable with this depth!

To obtain a more quantitative measure of these unusual results, the NIXSW profiles were fitted using the *XSWfit* routine [6], which is widely used in NIXSW analysis. Comparison of the data collected for thick Mn films using photoemission monitoring and Auger LVV monitoring was used to quantify the non-dipole contribution to the photoemission using the Q factor [7]. The profile obtained by these fitting routines is shown superimposed on the data in Figure 2. The routine extracts two parameters from the profile; the coherent position and the coherent fraction. For occupation of a single adsorption site, the coherent position is the position of the absorbing atom normal to the planes giving the X-ray reflection in units of the substrate plane separation. In this case, the coherent fraction would be an order parameter representing the fraction of atoms participating coherently in the reflection. Therefore, for the Cu substrate, it is expected that the coherent position will be 1.00 and the coherent fraction close to this, usually around 0.85. When more than one absorber site is present, the situation is more complex. If two sites are present, then the extracted coherent position will lie with appropriate weighting between the positions of the two sites and the coherent fraction will be

reduced. The way that these parameters are combined for two or more sites can be modelled in a simple mathematical way using the Argand plane description pioneered by other workers [8].

The fits to the data from the $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure are shown superimposed as solid lines in Figure 2. The coherent parameters extracted from these fits are shown in table 1.

Several statements may be made immediately. Firstly, the non-zero coherent fraction for Mn in the $[-111]$ reflection indicates a *commensurate* structure, or at least shows that not all of the Mn is involved in an *incommensurate* structure. Secondly, the low coherent fraction for Cu in the $[111]$ reflection, 0.64 rather than the expected 0.85, shows that the Cu atoms are in at least two different sites, one of which may be the expected substrate continuation.

Alternatively, some of the Cu atoms may be in a continuum of sites with a slightly different z-spacing from the bulk. Thirdly, as indicated above the anomalously large coherent position for Cu in the $[111]$ reflection, 1.21 rather than the expected 1.00, shows that the site with the highest occupation is displaced normal to the surface compared with the position of the plane in the bulk of the substrate. This displacement cannot involve just the top one or two layers, as the number of Cu layers contributing to the measurement goes well into double figures.

The high coherent position may indicate a uniform expansion of the top few layers of the crystal. If this were the case, successive layers would be at incrementally increasing site positions relative to the bulk and the coherent fraction would be reduced to reflect the large number of “sites”. If a large amount of this expanded lattice were sampled, then the coherent fraction would be zero. However, the finite sampling depth of photoemission could result in a reasonably high coherent fraction, if the expansion were small. The combination of the large coherent position and moderate reduction in coherent fraction indicate that a large fraction of the Cu surface is displaced outwards together while maintaining a reasonably bulk-like inter-plane spacing.

There are two possible explanations for the anomalous value of the coherent position of the Cu atoms as seen in the [111] reflection. The first is that the Cu and Mn may have formed a thick surface alloy, either ordered or dilute disordered, that has altered the surface to a comparatively large depth resulting in a surface layer with a modified structure. The second possibility is that the formation of the structure by annealing in the presence of adsorbed Mn or the sequential nature of the deposition process has disrupted the substrate by inducing stacking faults. Given that the two elements do not form bulk ordered alloys, then the latter is more likely, possibly caused by small amounts of Mn dissolving into the substrate.

The reduced Cu [111] coherent fraction indicates that either there is significant disorder, that there are two sites, or that there is a continuum of systematically displaced sites. The existence of multiple sites is most likely as there must be some contribution from Cu atoms on their normal lattice sites. Assuming this to be true and assuming only one other site, the best fit to the coherent parameters is obtained with 25% of the Cu signal being from atoms on their expected site and the remaining signal being due to atoms on a site with z distance of 1.26 (or 2.63 Å). This would be approximately equivalent to Cu stacking in an “atop” site, but further evidence relating to the possibility of different site is given below. Alternatively, the data fit a continuum of sites with a 2% expansion in z -spacing over bulk Cu expanding to 20 layers. Obviously the expansion and depth are correlated parameters allowing some variation in these values.

To obtain further information about the position of the Cu atoms, the coherent parameters for the [-111] reflection should be considered. Owing to the geometry of the vacuum system, the sampling depth for the [-111] reflection is similar to that for the [111] reflection. The key feature of the [-111] reflection is the low coherent fraction. Assuming the 25% signal in the [111] reflection to be due to the Cu atoms in their normal site, then it is impossible to fit the [-111] coherent parameters with only two sites without invoking a large amount of disorder.

They are easily fitted using a minimum of three sites but the parameters of these sites cannot uniquely be determined. However, it is important to note that the coherent position of close to 1 for the $[-111]$ reflection rules out the possibility of extensive occupation of an atop site, but instead indicates that a stacking sequence similar to fcc is maintained but with a displacement outwards. Although the $[-111]$ coherent position is consistent with a uniform 2% expansion over 20 layers as for the $[111]$, this model would produce a coherent fraction for the $[-111]$ that would be higher than for the $[111]$, the opposite to that found.

In combination, the two reflections show that the Cu surface atoms do not continue their normal stacking sequence, that there is a small lattice expansion or at least one stacking fault or interface with a spacing of 25% larger than the bulk and that above this the Cu atoms are in at least two different sites. This information is consistent with either an alloy or a faulted structure. If there is an ordered Cu and Mn surface alloy, then this structure cannot be simple substituted fcc and it must form a buried interface with the substrate. If there is a faulted structure, the stacking fault cannot be a simple one like the occupation of an “hcp” site rather than “fcc” but one that involves a displacement normal to the surface. Above this stacking fault the Cu atoms must occupy at least two sites as might be obtained by either twinning or by the presence of two such faults. Note that the atomic radius of Mn is larger than that of Cu, but the presence of one buried layer of Mn would not produce the required displacement and there is insufficient Mn present for two such layers.

Turning to the Mn profiles, the low coherent fractions rule out the existence of a unique site. The $[111]$ reflection is consistent with two sites arranged approximately equally in spacing around the coherent position of 1.27. The $[-111]$ reflection may also be fitted with two sites either side of the coherent position. Therefore, whatever the structure is there must be at least two different sites for the Mn. One may be associated with the $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure and the other with the deep modification of the surface, or they may both be

associated with a structure that is responsible for both the superstructure and the normal displacement. The Mn coherent positions are consistent with participation in a dilute alloy to slightly less than the full depth sampled. What is quite striking about the values presented in Table 1 is that the coherent positions and fractions of both Cu and Mn behave in a similar way, indicating that they are in similar environments in the altered layer.

The structure of this system is clearly complex. It is tempting to think of the large-scale modification of the surface as a true ordered surface alloy with an epitaxial structure different to fcc copper to such an extent that it results in two different sites for each element. However, a simpler explanation is that there is a surface Mn/Cu structure that gives the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure and that excess Mn introduced by the deposition process has induced sub-surface stacking faults or a small subsurface lattice expansion. The introduction of stacking faults, dependent on the sample deposition/cleaning history has been observed in other systems such as $\text{Ag}(111)(\sqrt{3}\times\sqrt{3})R30^\circ\text{-Sb}$ where the stacking fault involves the occupation of the wrong hollow site in a subsurface layer [9]. In the case of Mn on $\text{Cu}(111)$, a stacking fault involving an incorrect hollow would not give the expansion, but a similar process may be involved.

Combining the NIXSW measurements with the LEED observations it is possible to comment on the three most likely explanations for the observed data. The first possible explanation is that the Mn adsorption caused a surface $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure but in addition has introduced at least one stacking fault in the Cu. Such a model is entirely consistent with the data, but would involve stacking faults that displace Cu planes perpendicularly to the surface. Such a stacking fault is unlikely, an (admittedly improbable) buried layer of atop coordination would provide the expansion required for the $[111]$ coherent position, but is inconsistent with the $[-111]$ coherent position and fraction.

The second possibility, an ordered surface alloy, would be consistent with the data provided that it had two sites for both Mn and Cu but was not too different from fcc. This structure would be responsible for the extra LEED spots and so must be six-fold or must comprise two domains of three-fold symmetry with a mutual angle of 60° . There are several problems with this model, however. The amount of Mn is not large enough to provide disruption to a sufficient depth unless the alloy is dominated by Cu. Additionally, in the bulk, Mn and Cu do not form ordered alloys, and the depth required must mean the alloy is effectively bulk in nature. The final problem is that the authors cannot find a model that fits the data.

The third model is that the annealing has enabled the Mn to diffuse into the bulk and form a dilute alloy. It is known [10] that dilute alloys (of around 5%) are fcc and have a lattice parameter that is expanded by a few percent relative to pure copper. An expansion of around 2% for 20 layers would be consistent with the [111] data but not the [-111] coherent fraction. In this model, there would need to be an ordered surface layer – a surface excess concentration - to give the $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure. The problem with this model is the [-111] coherent fractions for Cu and Mn, which should be higher than for the [111] reflection. This could be explained by some limited lateral expansion in the lattice, possible with dislocation faults to prevent the surface becoming completely incommensurate with the lattice. Alternatively, the [-111] coherent fraction may be reduced by a fraction of fcc twinning in the altered layer. The net [-111] coherent fraction of the second domain would be zero. This would have the dual effect of reducing the [-111] coherent fraction and changing the LEED pattern to have a six-fold component, as observed. This final model must be considered the most probable, but the data do not enable the three models to be confidently distinguished.

Summary

Dosing and annealing Cu(111) with Mn in instalments forms an apparently commensurate $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure but disturbs the substrate to a significant depth, probably creating a dilute disordered alloy with a surface excess concentration, a thick ordered surface alloy, or inducing stacking faults in the subsurface. The correct answer cannot be confidently determined from these data alone, but the dilute alloy is the most likely. In the altered layer there are at least two different Cu sites and two different Mn sites or a continuum of sites due to a slightly expanded lattice.

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Figure Captions

Figure 1: Low energy electron diffraction pattern for the Cu(111)- ($\sqrt{3}\times\sqrt{3}$)R30°-Mn superstructure.

Figure 2: Normal incidence X-ray standing wave profiles for the Cu(111)- ($\sqrt{3}\times\sqrt{3}$)R30°-Mn.

The left shows the profiles for Cu and the right for Mn. The top shows the [111] reflection and the bottom the [-111] reflection. The broken line in (a) shows the NIXSW profile to be expected from both the [111] and [-111] reflection from the Cu(111) substrate.

Tables

Table 1: The coherent parameters determined from the curves shown in Figure 2.

Absorbing atom and reflection	Coherent position, P_c	Coherent Fraction, F_c
Cu [111]	1.21 ± 0.05	0.64 ± 0.05
Mn [111]	1.27 ± 0.05	0.51 ± 0.05
Cu [-111]	1.08 ± 0.05	0.34 ± 0.05
Mn [-111]	1.04 ± 0.05	0.25 ± 0.05

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Figure 1

(a) Cu [111] reflection

(b) Mn [111] reflection

(c) Cu [-111] reflection

(d) Mn [-111] reflection

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Figure 2