

Controlling the coexistence of structural phases and the optical properties of gallium nanoparticles with optical excitation

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We have observed reversible structural transformations, induced by optical excitation at $1.55 \mu\text{m}$, between the β , γ and liquid phases of gallium in self-assembled gallium nanoparticles, with a narrow size distribution around 50 nm, on the tip of an optical fiber. Only a few tens of nanowatts of optical excitation per particle are required to control the transformations, which take the form of a dynamic phase coexistence and are accompanied by substantial changes in the optical properties of the nanoparticle film. The time needed to achieve phase equilibrium is in the microsecond range, and increases critically at the transition temperature.

We report that the coexistence of different crystalline and disordered phases in nanoparticles can be controlled by optical excitation in a *controllable, continuous and reversible* fashion. This has been observed in nanoparticles of polymorphic elemental gallium. Shifts in the balance between phases are accompanied substantial changes in the optical properties of the nanoparticle film. The light-induced transformations display phenomenological features typical of 1st-order Ehrenfest phase transitions (such as a reflectivity hysteresis) but simultaneously display characteristics of 2nd-order transitions (such as critical dependencies on temperature of the ‘susceptibility’ and relaxation time of the stimulated response). Our study is motivated by a desire to understand the exciting physics of phase equilibria in nanoparticles [1, 2, 3] and in particular in metallic nanoparticles, which have the potential to play a key role in future highly integrated photonic devices as the active elements of waveguiding [4] and switching [5] structures.

We studied light-induced structural transformations in gallium nanoparticles by monitoring the optical reflectivity of nanoparticle films. The particles, typically 50 nm in diameter with a relatively narrow size distribution ($\pm 14 \text{ nm}$), were prepared on the tips of silica optical fibers, using the recently developed light-assisted self-assembly technique [6, 7]. This process produced a nanoparticle film on the fiber’s core ($9 \mu\text{m}$ in diameter) comprising $\sim 2 \cdot 10^4$ nanoparticles. Phase transitions in the nanoparticles were stimulated by a 1.4 mW , $1.55 \mu\text{m}$ diode laser launched into the fiber. Its output was modulated with 50% duty cycle at 6.2 kHz providing an average excitation power of about 22 nW per nanoparticle. Another 0.4 mW cw diode laser operating at $1.31 \mu\text{m}$ and phase-sensitive detection apparatus were used to monitor the reflectivity of the film. The detection system had an overall bandwidth of 300 kHz .

The nanoparticle film’s reflectivity shows a very wide ($> 100 \text{ K}$) hysteresis, with two distinct steps, at $T'_0 \sim 233 \text{ K}$ and $T_0 \sim 253 \text{ K}$, in the rising temperature part of the

cycle (Fig. 1a). The presence of these steps indicates that there are two structural phase transitions and therefore that either the nanoparticles undergo a transition from one solid phase to another and then from that phase to the liquid, or that two solid phases coexist at low temperatures and undergo the transition to liquid at different temperatures. Analysis of gallium’s phase diagram [8] and results from energy-dispersive x-ray diffraction studies of gallium nanoparticles [9] suggest that in the present case the solid phase with the highest melting point is β -gallium, and that the other solid phase is γ -gallium.

The presence of pump excitation at $1.55 \mu\text{m}$ changes the reflectivity of the nanoparticle film by several percent in a reversible and reproducible fashion. The magnitude Δ of the induced reflectivity change (Fig. 1b) has a non-zero value at all temperatures, with pronounced peaks that coincide with the steepest parts of the corresponding reflectivity versus temperature plot. With increasing temperature, and the relative phase shift (Fig. 1c) between the pump modulation and the change in probe reflectivity $\phi \approx 0$ across the whole range from 90 K to $\sim 253 \text{ K}$ (T_0), indicating that the reflectivity responds quickly to optical stimulation, with relaxation times smaller than $10 \mu\text{s}$. At T_0 and T'_0 , Δ increases by a factor of ~ 8 , and above T_0 the phase shift ϕ becomes negative. Above $\sim 255 \text{ K}$, $\phi \approx -180^\circ$, meaning that optical excitation actually reduces the reflectivity of the nanoparticles in the molten phase. The relaxation time τ of the nonlinearity increases steeply in the proximity of the peak with scaling dependence $\tau \propto (T_0 - T)^{-1.7}$, while the magnitude of the response in the same temperature range follows $\Delta \propto (T_0 - T)^{-1.5}$ (Fig. 2). Remarkably, the phase shift between the pump modulation and the probe reflectivity change remains almost zero at T'_0 , indicating that the response and relaxation times remain short ($< 10 \mu\text{s}$). With decreasing temperature, the pump and probe remain in anti-phase until $\sim 180 \text{ K}$, then ϕ returns to zero by $\sim 150 \text{ K}$. A small, smooth peak is seen in Δ at the re-crystallization temperature T_0^* .

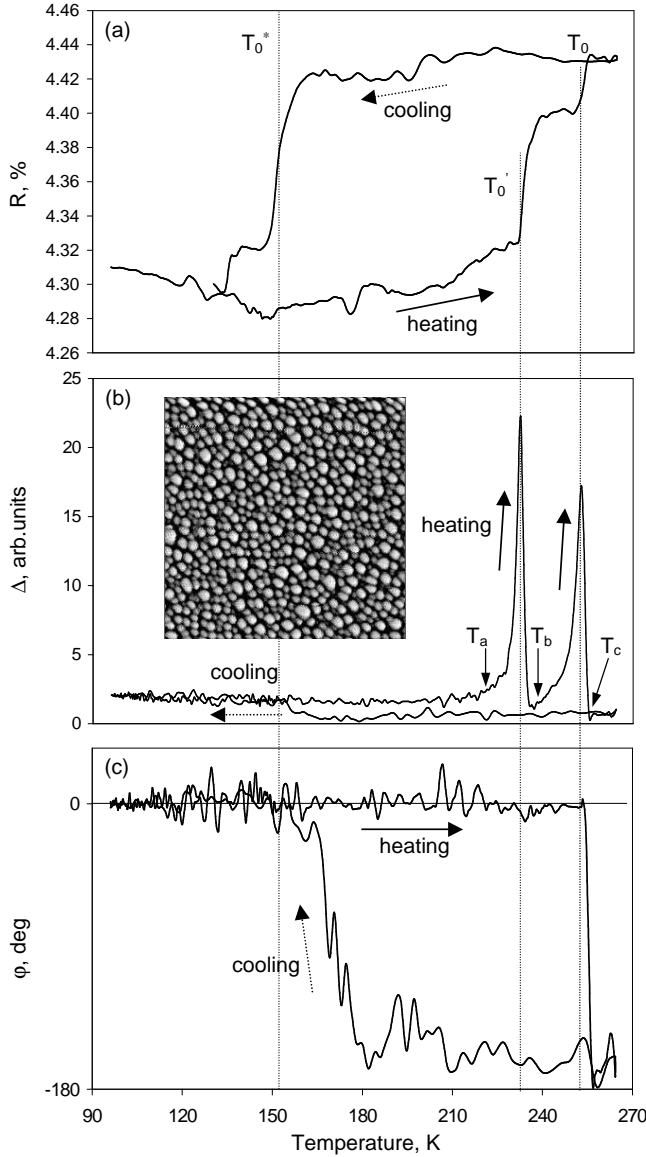


FIG. 1: Temperature dependencies of (a) Reflectivity, (b) pump-induced reflectivity change Δ , and (c) phase-shift ϕ between pump excitation and probe response for gallium nanoparticles on the core of a single mode optical fiber. The inset to (b) shows an atomic force microscope image of a $2 \times 2 \mu\text{m}$ area of nanoparticles.

The phenomenological picture seen here is unusual and is quite different from what is normally observed in the bulk where first order phase transitions are characterized by a discontinuous change in the state of the body, effected by means of a sudden rearrangement of the crystalline lattice. Many features of our experimental results may be explained by consideration of the fact that under the confined conditions of the nanoparticle geometry, there is a continuous dynamic coexistence of structural forms in the nanoparticles. Such behavior has been studied theoretically for small clusters, and it was predicted

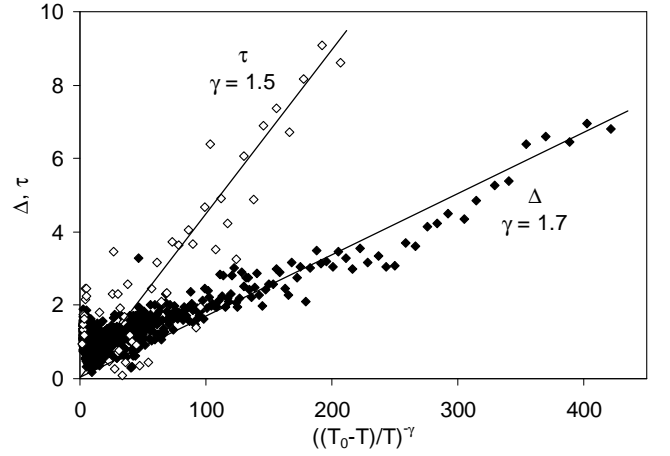


FIG. 2: Pump-induced reflectivity change Δ and relaxation time τ as scaling functions of temperature.

that there would be a temperature interval wherein two different phases coexist [1, 2]. The surface of a particle, where atoms have fewer nearest neighbors than internal atoms, becomes very important and acts as a boundary at which transformation processes can start. We believe that this concept is largely applicable to the present case and it brings us to a model in which we consider an ellipsoidal nanoparticle with a core in one structural phase covered by a homogeneous ‘shell’ of another phase. In the simplest case of a phase transition to the melt, the light-induced behavior of such a particle would be analogous to the temperature-driven ‘surface melting’ effect that has been seen in lead nanoparticles [10] and found to be thermodynamically reversible within a narrow temperature range [11]. In the presence of light, the equilibrium position of the phase boundary, or to put it another way, the thickness of the surface layer, will be determined by both temperature and light intensity. At a certain temperature T_a below the phase transition point T'_0 the influence of light on the surface layer’s thickness becomes apparent as optical excitation changes the reflectivity of the film (see Fig. 1b). With increasing temperature or level of optical excitation, the surface layer’s thickness increases until the transformation of the core to the ‘surface’ phase is completed. When, at T_b , the core of the particle is fully consumed by the new phase the nanoparticle becomes stable against a return to the old phase because this would require the creation of a nucleation center. However, if the temperature or level of optical excitation is reduced *before* the transformation to the new phase is complete, i.e. while a nucleus of the old core phase is still present, the transformation is reversed and the skin layer shrinks to an appropriate equilibrium position. Thus, reversibility is provided in the temperature range between T_a and T_b . This whole process is then replicated around the next phase transition temperature T_0 (see Fig. 3a). From the standpoint of phase

transition theory the observed effect shows some features of second-order transitions: the thickness of the surface layer is characterized by the correlation length of near surface fluctuations $\xi \propto (T_0 - T)^{-\nu}$. The susceptibility is then a scaling function of the correlation length: $\chi = (\delta\eta/\delta h)_T \propto (T_0 - T)^{-\gamma_1}$, where $\gamma_1 = 1.5$ in our experiment. When the optical excitation is terminated, the skin layer retreats and the reflectivity is restored to its original level. Like the susceptibility, the relaxation time has scale-invariant form, i.e. $\tau \propto (T_0 - T)^{-\gamma_3}$, where $\gamma_3 = 1.7$ in our experiment. The longer relaxation times near the phase transition temperatures result from the increased thickness of the surface layer and reduced velocity of the interface between the phases. In terms of Landau theory this situation may be described by taking the free energy of a particle to be a polynomial function of the order parameter $\psi \sim r^{1/3}$, where r is the radius of the solid core within a particle of radius R . As is usual in the vicinity of a second order phase transition, the value of the order parameter will characteristically be proportional to $(T_0 - T)^{1/2}$, giving $r \propto (T_0 - T)^{1.5}$. The reflectivity of the nanoparticle film will then, to a first approximation, be proportional to the volume of the molten phase: $V_m = 4\pi R^3[(R-r)/R - ((R-r)/R)^2 + ((R-r)/R)^3/3] \sim t^{1.5}$, where $t = -(T - T_0)/(T_0)$, thus producing correct estimates for the experimental values of the critical indices. Intriguingly, the relaxation time for the first transition at T'_0 is much shorter than for the second one at T_0 . This may be an indication that the first transition occurs between two solid phases and would be consistent with the thermodynamic argument that the enthalpic and entropic contributions to the Gibbs free energy appear to enter differently into the kinetics of solid-solid and solid-liquid transitions because of the difference in the configurational and vibrational space available in the solid and liquid phases [12].

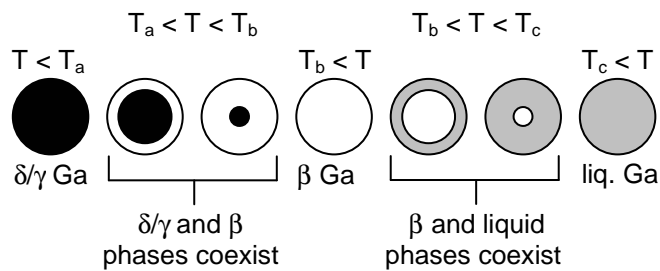


FIG. 3: Shell model for a solid-solid-liquid series of structural transformations occurring with increasing temperature in gallium nanoparticles.

The strength of the phase coexistence concept is supported by calculations of the optical properties of gallium nanoparticle films on a dielectric substrate performed using a recently developed effective-medium model for densely packaged nanoshells [13]. For the purposes of our calculations, the dielectric constants of β - and γ -

gallium, which are much closer to those of a free-electron metal than those of the α phase, were estimated by using the damping constant in Drude's free-electron model as a fitting parameter to produce the nanoparticle film reflectivity levels shown in Fig. 2a. These calculations (also detailed in Ref. [13]) confirmed that the presence on each nanoparticle of a shell just a few nanometres thick in a phase different from the core can produce a change in reflectivity sufficient to explain our experimental data.

A thermally activated transition due to laser-induced heating can explain certain characteristics of the effect. For instance, by assuming a local light-induced temperature increase of 0.42 K , one can derive a good facsimile of the experimental peaks in Δ at T'_0 and T_0 from the reflectivity data in Fig. 1a. However, there are serious discrepancies between the results of this thermal model and the experimental results, primarily at temperatures more than a few degrees below the peaks, where the observed effect is larger than predicted. The thermal model also fails to explain important details of ϕ 's dependence on temperature. This suggests that another, temperature-independent, non-thermal excitation mechanism is also contributing to the effect. This mechanism may be especially important for gallium which is known to have covalent bonds within some of its crystalline structures [14]. The covalent bonds' absorption line encompasses the pump wavelength [15], so optical excitation may result in bonding-antibonding transitions, which destabilize the structure [16]. A 'defect' or 'inclusion' of a new phase is thus created, changing the optical properties of the 'host' phase at temperatures far below its transition point. Furthermore, the latent heat of transition from the defect-containing structure to a new phase is reduced in proportion to the number of defects. The latent heat controls the balance between phases [17], so this defect creation eventually shifts the phase equilibrium and promotes the formation of a thicker layer of the new phase without any increase in temperature. This process could provide an additional, non-thermal contribution the peak at T_0 and T'_0 . Such 'optical melting' mechanisms, proceeding through light-induced destabilization of the crystalline bond structure, have been analysed previously for gallium [18] and selenium [19].

In conclusion, we have found that light can stimulate reversible structural transitions in gallium nanoparticles that belong to a novel class of surface-driven excitation-induced phase transitions and have some striking similarities with a transition recently observed in superfluid helium droplets [20] and a transformation believed to occur in confined superconductors, wherein the existence of a 'boundary phase', characterized by spontaneous fluctuational nucleation of short-lived vortices is critical [21]. If there are substantial differences between the optical properties of the phases involved, as there are in gallium, this type of transition provides a new means of obtaining a large optical nonlinearity, which may be used to

control light with light in nanostructured materials such as ‘plasmon waveguides’ made from arrays of metallic nanoparticles.

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- [1] B. M. Smirnov, Phys. Scr. **50**, 427 (1994).
 - [2] R. S. Berry, J. Jellinek, and G. Natanson, Phys. Rev. A **30**, 919 (1984).
 - [3] R. S. Berry and B. M. Smirnov, J. Chem. Phys. **113**, 728 (2000).
 - [4] J. R. Krenn, A. Dereux, J. C. Weeber, E. Bourillot, Y. Lacroute, J. P. Goudonnet, G. Schider, W. Gotschy, A. Leitner, F. R. Aussenegg, et al., Phys. Rev. Lett. **82**, 2590 (1999).
 - [5] N. I. Zheludev, Contemp. Phys. **43**, 365 (2002).
 - [6] K. F. MacDonald, V. A. Fedotov, S. Pochon, K. J. Ross, G. C. Stevens, N. I. Zheludev, W. S. Brocklesby, and V. I. Emel’yanov, Appl. Phys. Lett. **80**, 1643 (2002).
 - [7] V. A. Fedotov, K. F. MacDonald, N. I. Zheludev, and V. I. Emel’yanov, J. Appl. Phys. **93**, 3540 (2003).
 - [8] L. Bosio, J. Chem. Phys. **68**, 1221 (1978).
 - [9] A. Di Cicco, Phys. Rev. Lett. **81**, 2942 (1998).
 - [10] R. Garrigos, P. Cheyssac, and R. Kofman, Z. Phys. D **12**, 497 (1989).
 - [11] K. F. Peters, Y. W. Chung, and J. B. Cohen, Appl. Phys. Lett. **71**, 2391 (1997).
 - [12] J. Y. Tsao, M. J. Aziz, M. O. Thompson, and J. . P. S. Peercy (????).
 - [13] V. A. Fedotov, V. I. Emel’yanov, K. F. MacDonald, and N. I. Zheludev, J. Opt. A: Pure Appl. Opt. **6**, 155 (2003).
 - [14] M. Bernasconi, G. L. Chiarotti, and E. Tosatti, Phys. Rev. B **52**, 9988 (1995).
 - [15] X. G. Gong, G. L. Chiarotti, M. Parrinello, and E. Tosatti, Phys. Rev. B **43**, 14277 (1991).
 - [16] Y. Siegal, E. N. Glezer, L. Huang, and E. Mazur, Annu. Rev. Mater. Sci. **25**, 223 (1995).
 - [17] R. Trittibach, C. Grutter, and J. H. Bilgram, Phys. Rev. B **50**, 2529 (1994).
 - [18] K. F. MacDonald, V. A. Fedotov, R. W. Eason, N. I. Zheludev, A. V. Rode, B. Luther-Davies, and V. I. Emel’yanov, J. Opt. Soc. Am. B **18**, 331 (2001).
 - [19] V. V. Poborchii, A. V. Kolobova, and K. Tanaka, Appl. Phys. Lett. **74**, 215 (1999).
 - [20] M. O. Kimball, M. Diaz-Avila, and F. M. Gasparini, *23rd International Conference on Low Temperature Physics* (Hiroshima, Japan, 2002).
 - [21] M. B. Sobnack and F. V. Kusmartsev, Phys. Rev. Lett. **86**, 716 (2001).