Distinct liquid phase in metal-cluster superlattice solids

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Variable temperature x-ray diffraction and differential scanning calorimetry experiments on the superlattice solids of alkanethiol protected silver nanoclusters show that the translational periodicity collapses around 398 K resulting in a liquid phase, which upon cooling, reverts into the parent crystalline phase. This reversibility is seen in a narrow temperature window of 400–448 K. If the heating is done above 473 K, the reversibility is lost, and the liquid in the cooling cycle freezes into a disordered phase. The stability of different phases, encountered in the experiments, is discussed in terms of a phenomenological free energy.

Monolayer protected clusters (MPC's), especially thiolate capped gold and silver quantum dots (QD's), are intensely investigated in the recent past.[1–4] Quantum dots capped with monolayers self-assemble to form superlattices in the solid state.[5] The question whether such a solid could possess a liquid phase is important, in order to classify them as molecular solids. In this paper we report experimental evidence for reversible transition of this solid to a liquid phase in a narrow temperature range. The stability of different phases has been understood in terms of a simple phenomenological Landau free energy.

Octadecane-, octane-, pentane-, and butanethiol protected silver clusters were synthesized by modifying[6] the method originally employed for gold clusters.[7] During the synthesis procedure, alkanethiol chains get grafted at the sulfur end onto the surface of the clusters. The clusters thus prepared are soluble in organic media and can be recrystallized repeatedly. We call silver clusters thus coated with octadecanethiol (ODT) as Ag-ODT clusters. We illustrate the observations specifically on Ag-ODT, although similar observations have been made with Ag clusters capped with other thiols. The core of such a cluster is crystalline Ag with faceted[2,8] surfaces providing specific sites for the alkanethiol chains to get attached. Inset I of Fig. 1 shows a schematic structure of the superlattice crystalline phase of such clusters at room temperature. The figure shows that the crystalline lattice arises out of the interaction of interpenetrating alkyl chain bundles assembled on the surface planes of the nanocluster.[5,6] Variable temperature x-ray diffraction (XRD) measurements using an X′ Pert-MPD Diffractometer with Cu $K\alpha$ radiation were performed on the sample spread on a metallic heating plate. The diffractograms in the range of 3–51° of 2θ were measured with a step size of 0.05°, each measurement taking 1000 s. The measurements were carried out rapidly compared to a typical single scan acquisition to avoid the potential x-ray induced damage of the thiolates[9] and consequently the patterns are noisier than a typical measurement. Earlier studies have shown that Ag clusters of average core diameter 4.0 ± 0.5 nm capped with alkanethiols form single phase superlattice solids which have been investigated by a number of techniques.[6] Figure 1(a) shows the x-ray diffractogram of

Ag-ODT sample as prepared at 298 K. The pattern shows low angle reflections in addition to the usual silver reflections at 38.5° and 44.6°. The low angle peaks from a solid composed of capped silver clusters[6] can only be due to its lattice. These reflections are observed up to a temperature of 398 K, indicating the stability of this phase of the material. Diffractogram taken at 423 K shows the near complete disappearance of the superlattice reflections [Fig. 1(b)]. Only the reflections of the parent Ag lattice arising from isolated clusters persist. Upon cooling from 448 K, almost all of the superlattice reflections are regained. However, only the parent silver reflections and no superlattice peaks are seen in a sample cooled from 473 K. Thus the data show that the nanocluster lattice melts below 423 K. This transition was further investigated over a temperature range of 123–473 K by differential scanning calorimetry (DSC) using a Netzsch PHOENIX DSC204 instrument with 10 mg of the sample encapsulated in an aluminum pan. Thermogravimetric measurements showed that there was no weight loss in this temperature window and thiolate desorption commences only above 540 K in these samples. Thus the transition seen in XRD is not due to thermal decomposition or desorption of the capped molecules. The chemical integrity of the monolayers throughout the heating process was further confirmed by variable temperature infrared spectroscopy.

In inset II of Fig. 1, we show a series of photographs of an 8 mm diameter pellet of the sample as a function of temperature: (a) the sample at 298 K, and (b) heated to 423 K when melting of the solid commences as evidenced by the disappearance of the sharp edges. The solid in immediate contact with the glass plate melts first and the liquid starts spreading. At 433 K, a clear liquid surface has been formed as seen in (c). Above this temperature, the liquid flows on the glass substrate. These pictures demonstrate that the material beyond 423 K behaves like a liquid.

In Fig. 2, we compare the DSC data of Ag-ODT under two experimental conditions. The sample was heated initially to 423 K and cooled back to 298 K (experiment 1), and heated to 473 K and cooled back to 298 K (experiment 2). In the heating cycle of the experiment 1, the DSC traces shows two transitions, the first around 335 K and the other at 405 K
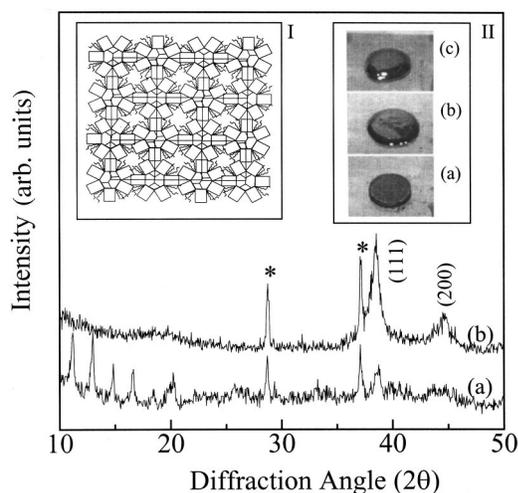
FIG. 1. Variable temperature x-ray powder diffraction patterns of Ag-ODT at (a) 298 K and (b) 448 K. Note the absence of the superlattice reflections (peaks below 22° 2θ) and the increase in intensity of the (111) and (200) reflections of bulk Ag. Inset I: A schematic structure of Ag-ODT at room temperature. The metal core is indicated by a hexagon, the column of organized alkyl chains assembled on each face of the cluster is represented by a rectangle and the unorganized alkyl chains by curved lines. Inset II: A series of photographs of an 8 mm pellet of the material at various temperatures: (a) 298 K, (b) 423 K, and (c) 433 K. At 423 K the photograph shows the disappearance of the sharp edges, suggesting a melting transition.

[Fig. 2(a)]. The first one is ascribed to the melting of the alkyl chain order, which has been ascertained independently by variable temperature infrared spectroscopy.[6] As a result of alkyl chain melting, the IR frequencies, especially those of the methylene modes become liquidlike,[10] the modes hardened by about 10 cm^{-1}. This is due to increased gauche conformations and is a characteristic signature of liquid alkanes.[10] The second transition at 405 K is ascribed to the melting of the cluster superlattice, in agreement with the XRD observations. The enthalpy of the superlattice melting is substantial which indicates a large cohesive energy[11] of the super structure. Upon cooling from 423 K, the transitions are again observed, however, the superlattice freezing enthalpy is considerably less than that of the melting. The alkyl chain freezing releases more energy presumably because of enhanced degree of order in the chain assemblies as compared to the starting material. In the starting material an arbitrary amount of disorder could have been frozen in; but during heating/cooling they possibly get annealed out. Increased interchain interaction on each cluster reduces the extent of superlattice assembly decreasing the enthalpy while cooling. Infrared spectroscopic investigations[12] have confirmed that the alkyl chains have attained increased order upon cooling as evidenced by the factor group splitting of the methylene wagging mode at 1460 cm^{-1} after repeated heating/cooling cycles.[13,14] Cooling also brings back the methylene vibrational frequencies to the characteristic values of crystalline alkanes. However, the binding sites of the thiol on the Ag clusters do not appear to be changed, as the *C-S* stretching mode remains unaltered. Figure 2(b) shows the DSC data in the experiment 2, both the transitions are seen while heating. However, in the cooling cycle, the superlattice freezing is not observed.
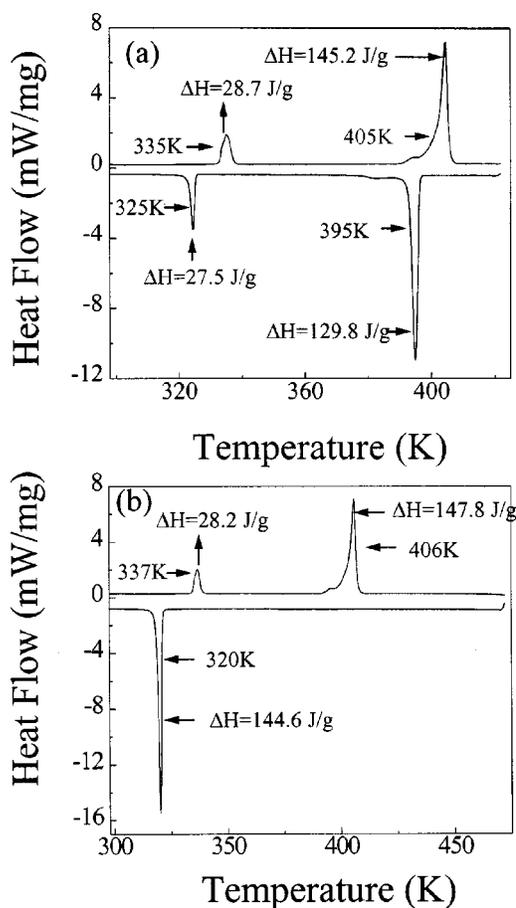

FIG. 2. Differential scanning calorimetric traces of Ag-ODT. (a) Experiment 1: heating to 423 K and cooling back to 298 K and (b) experiment 2: heating to 473 K and cooling back. Transition temperatures and enthalpies are marked.

The results can be summarized as follows. The superlattice has two distinctly different liquid forms: one having no alkyl chain order (experiment 1, beyond the second peak in DSC heating curve) and another with alkyl chain order (below the peak in DSC cooling curve of experiment 2). These liquid forms are schematically illustrated in Fig. 3(a). Upon melting the superlattice, the ordering of the alkyl chain assembly has been lost [Fig. 3(a), left]. There is, however, another low temperature phase, where the superlattice order is absent, even though the order within the alkyl chain body has increased [Fig. 3(a), right].

Having the experimental evidences for the existence of liquid phases in Ag-ODT superlattice, we propose a simple phenomenological Landau free energy[15] to understand the stability of the different liquid phases, shown schematically in Fig. 3(a). It is well known that the translational order of a crystalline solid can be described by means of the Fourier components of the spatial density distribution at the reciprocal-lattice vectors (RLV's) of the appropriate crystalline symmetry.[16] In the present case, the only Fourier component ρ, corresponding to the smallest RLV's of the simple cubic lattice is employed to describe the superlattice translational order parameter. While formulating the free energy as a polynomial in ρ the coefficients of different powers in ρ are obtained by counting the number of closed polygons that can be formed out of the smallest RLV's,
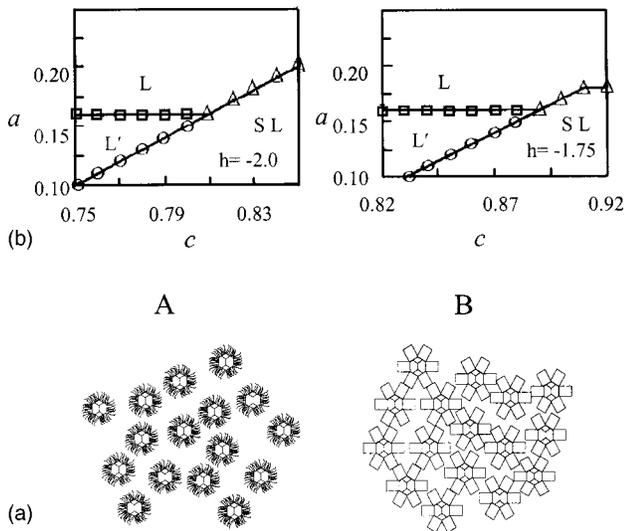
FIG. 3. (a) Schematic illustration of the phase transition of the superlattice: Ag-ODT (left) at higher temperature, and (right) cooled back to room temperature as in experiment 2 (see the caption of Fig. 1). (b) The phase diagrams derived from the mean-field phenomenological free energy for different values of h with $b = 1.22$, $d = 2.0$, and $k = -15$ (see text). Note the difference in the horizontal scales in the two cases. All the phase boundaries are first order.

namely, $\{\cos 2\pi(\pm x, 0, 0), \cos 2\pi(0, \pm y, 0), \cos 2\pi(0, 0, \pm z)\}$. The free energy calculated in this manner can have only even powers of ρ and given by, $F_{\text{trans}} = 3(1-c)\rho^2 + (90/12)\rho^4 + (1860/30)\rho^6$, where c is the magnitude of the intercluster direct correlation function[17] in the liquid state at the smallest RLV's.

Since the sulfur ends of the alkanethiol chains get grafted onto the surface of the silver clusters very strongly, the anchoring directions depending on the crystallographic plane onto which the chains are grafted, is taken to remain unaltered throughout the temperature range of the experiments. Hence, within the temperature range under consideration, the excitation associated with the detachment of the grafted end of the chains, and the elastic cost of free energy associated with the change in the anchoring directions can be ignored. We further assume that the surface forces responsible for this grafting are fairly short ranged, so that the remaining part of the chain can show liquid crystalline order depending on the temperature. Consequently, we describe the rotational states of the alkanethiol chains, barring the grafted part, by a liquid crystalline order parameter (Ref. 17) S, which characterizes the orientational order of the chains with respect to a preferred axis, determined by the anchoring direction. The free energy in powers of S is known to have a form (Ref. 17) $F_{\text{rot}} = (a/2)S^2 - (b/3)S^3 + (d/4)S^4$, where a, b, and d are phenomenological parameters.

The coupling between S and ρ is introduced from the symmetry considerations. Note that the free energy permits only even powers of ρ. Since the alkyl chains, excepting the grafted part are the same irrespective of whether they are looked at from the cluster metal surface to the top or reverse (up-down symmetry), the lowest order coupling can only involve S^2, so that to the lowest order, the coupling term in the free energy: $F_{\text{couple}} = hS^2\rho^2 + kS^2\rho^4$, where h and k are phenomenological parameters.

The total free energy, $F = F_{\text{trans}} + F_{\text{rot}} + F_{\text{couple}}$, is to be minimized with respect to ρ and S to find the equilibrium phases in the space of a and c, with given choice of b, d, h, and k. The instability in ρ is triggered by the rotationally ordered state, $S \neq 0$), because the effective intercluster correlation given by the coefficients of the quadratic power of ρ in F, gets enhanced to $c' = 3(1-c) + |h|S^2$. The enhancement implies a stronger intercluster interaction in the mean-field sense[18] and can be regarded as a signature of interdigitation, which brings the clusters closer together. The resulting phase diagrams are shown in Fig. 3(b). We note that for high values of c and low values of a, the superlattice (SL) phase characterized by $\rho \neq 0$ and $S \neq 0$, is stable. As one goes to a higher a for a given c, one encounters a liquid phase (L), in which both the order parameters are zero. For the lower values of a and c, however, one encounters a region of exotic liquid phase L$'$, having no superlattice order, even though $S \neq 0$. The transition across the line SL-L is found to be first order. This is not surprising, for the transition is driven by S which itself grows discontinuously due to the presence of the cubic power in F_{rot}. So is the case for L-L$'$ transition line. However, the SL-L$'$ transition line could be either first order, or continuous, or consisting of both having a tricritical point on the phase boundary, depending on k. Figure 3(b) shows a remarkable sensitivity of SL-L and SL-L$'$ phase boundaries to the phenomenological parameters; a decrease in $|h|$ increases the stability of the liquid L and L$'$) phases.

In order to draw correspondence with the experimental observations, we note that c decreases, while a increases as the temperature increases. Hence, with increasing temperature, as found in the experiments, the theory shows a thermodynamic phase transition from SL phase to a L phase. Note that the transition is reversible. However, a possibility of L$\rightarrow$L$'$ transition, as in the cooling cycle of experiment 2, cannot be ruled out due to the sensitivity of SL-L and SL-L$'$ phase boundaries to the phenomenological parameters which are strongly dictated by the experimental conditions and the material parameters. It is worthwhile to point out that the melting of the superlattice proceeds via the melting of the alkyl chains in the experiments. Such an instability cannot occur in the present theory, simply because ρ is driven by S. The shape anisotropy of the clusters themselves, hitherto neglected, leads to an additional order parameter describing the intercluster rotational order. The coupling of this additional order parameter with ρ may stabilize the $\rho \neq 0$ phase, even if $S = 0$. Work is progressing in this direction.

In conclusion, we show that MPC silver cluster superlattice has well defined liquid state.[19] This suggests that the constituent clusters, with their protective monolayers behave like molecular units. As is well known, the intermolecular interaction governs the phase behavior of molecular solids. It is useful to compare the present situation with that of the fullerene C_{60} system. The C_{60} solids do not show any high temperature liquid phase. This is related to the fact that due to the nature of the interparticle interaction potential, the triple point of such systems falls above the gas-liquid critical point.[20] This clearly makes it important to probe the intercluster interaction in the present case, although this is highly nontrivial due to the presence of the encapsulating chains. Such studies would be of immense help to build up a more

microscopic understanding of the stability of the different phases. It will be very interesting to observe the direct transition between the superlattice phase to the exotic liquid phase, and to assess the order of such a transition.

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[19] It is worthwhile pointing out that similar observations are obtained for other Ag clusters. For Ag-OT (corresponding to octanethiol capped Ag clusters), for instance, the alkyl chain melting shows up at 258.7 K, as observed in isolated octanethiol capped gold clusters studied previously (Ref. 12). Further, the melting of Ag-OT superlattice proceeds through multiple steps in a narrow window of temperatures, centered on 390 K, attributed to the presence of different conformers in the alkyl chain assembly. This may also account for the width of the DSC peaks.

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