Phase transition in an ordered ensemble of 8-atom indium clusters (melting temperature and enthalpy)

Yu. A. Alekseev, V. N. Bogomolov, V. A. Egorov, V. P. Petranovskiĭ, and S. V. Kholodkevich

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Moscow

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A phase transition (PT) is observed at $T \sim 235$ K in an ensemble of 8-atom clusters of In in NaA zeolite, corresponding to melting of In particles, whose temperature is decreased due to the size effect. The measured enthalpy of the PT is two orders of magnitude smaller than the enthalpy of melting of bulk indium.

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Experimental studies of the thermodynamic characteristics of small metallic particles and microclusters are primarily concerned with the dependence of the melting temperature (T_m) on their size. On the other hand, the energy characteristics of this transition have not been studied because of the technological peculiarities of the specimens used (small volume concentration and considerable spread in particle size), although these characteristics are essential for constructing a thermodynamic theory of small particles.

Apparently, only the creation of ensembles of size-calibrated microclusters in cavities of zeolites (and other regular matrices) permits obtaining macroscopic samples for determining the energy characteristics of thermal transformations in ultradispersed particles, since it provides high concentration of the clusters being studied ($\sim 5 \times 10^{20}$ cm^{-3}). Melting of 9-angstrom clusters of Hg, Sn, and Ga was first observed in zeolites in Ref. 1. The size dependence of T_m of In particles up to sizes ~ 60 Å was studied in Ref. 2.

We studied the thermal characteristics of a lattice of 8-atom clusters of In in NaA zeolite (the technology for obtaining them, the composition, structure and optical properties of NaA–In_8, crystals are described in Ref. 3) in the temperature range 100–650 K using the Perkin Elmer DSK-2 apparatus. We were able to measure T_m and to determine for the first time the heat of the phase transition.

Figure 1 shows the temperature dependences of the differences in heat capacity $\Delta c_p = c_p^1 - c_p^2$, where c_p^1 and c_p^2 are heat capacities[1)] of the specimen being studied and a reference (quartz), respectively, for different rates of heating: 0.31 K/min (curve 1) and 10 K/min (curve 2). In dehydrated NaA, a PT was not observed in the entire range studied, so that the observed endothermal peak in curve 1 could be attributed only to the PT in the lattice of In_8 clusters. As the rate of heating increases, i.e., the sensitivity increases, one more peak appears in the specific heat (curve 2).

As shown in Ref. 1, existing theoretical models of the mechanism of melting of small particles permit describing the decrease in T_m with a decrease in their size by the

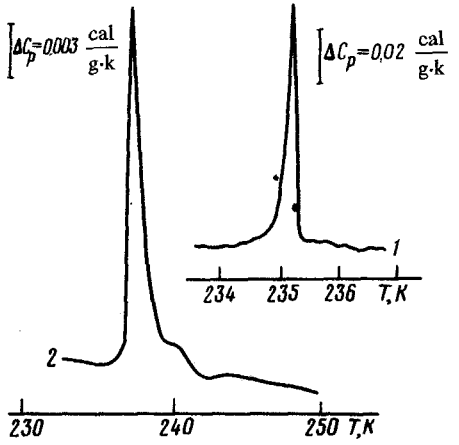

FIG. 1. Temperature dependence of the differential specific heat ΔC_p and NaA–In_8 for heating rates: 0.31 K/min (1) and 10 K/min (2).

relation

$$T_m / T_0 = 1 - D_{\text{lim}} / D \,, \tag{1}$$

where T_0 is the melting temperature of the bulk metal, T_m is the melting temperature of particles with diameter D, D_{lim} is a parameter that describes the limiting size of a particle which is liquid even at absolute zero. Different theoretical models give different values of D_{lim} and, in addition, according to Ref. 1, the theory of melting of surface layer[4] gives values of D_{lim} that are closest to the experimental values (for In $D_{\text{lim}} = 5.5$ Å). On the basis of our experimental data, we obtained from Eq. (1) $D_{\text{lim}} = 4$ Å, i.e., a quantity of the order of atomic dimensions. The value obtained for D_{lim} leads, for 220 Å In particles, to $T_m = 422$ K, which agrees well with the experimental value 408 ± 8 K.[2] This clearly indicates that there is a genetic relation between the PT observed by us (curve 1) in the lattice of 8-atom In clusters and the melting of bulk indium.

We note that in all theoretical models the quantity D_{lim} depends on several physical quantities: the latent heat of melting, the densities of the solid and liquid phases, and the surface energy of separation of different phases. The model chosen leads to a definite relation between these quantities, so that the value of D_{lim} is a criterion for the correctness of the model chosen. However, it is difficult to analyze the experimental data for large particles due to the comparative smallness of the changes in T_m, while in ensembles of small particles obtained by the standard methods difficulties arise due to the considerable broadening of PT resulting from the spread in the particle size. As a result, it is undoubtedly worthwhile to determine D_{lim} for an ensemble of strictly calibrated particle sizes in order to estimate the applicability of different theories.

The average number of atoms in In clusters in the cluster crystal NaA–In_8 is 8.02 ± 0.04.[3] The regularity of the sizes and positions of clusters in the matrix of the system studied at such high cluster concentrations (5×10^{20} cm^{-3}) is apparently the reason for the fact that the observed peak in the pressure has a half-width of only 0.16 K (curve 1). The enthalpy of melting determined from the area of the peak is

$\Delta H_f = 0.065 \pm 0.005$ cal/g (5.2×10^{-16} erg/atom). [For bulk In, $\Delta H_f = 6.8$ cal/g (5.4×10^{-14} erg/atom).] Such small heats of transition could be the reason for the high sensitivity of microclusters to external perturbations.[5]

Melting of a massive substance is usually assumed to be a breakdown of long-range order (i.e., disappearance of translational invariance). However, short-range order also breaks down with melting (coordination polyhedron: bond length, valence angle, coordination number). For example, due to thermal activation, the cubic octahedron of the fcc lattice of metals transforms under melting into an icosahedron[6] (the interatomic distance in this case changes by only a factor of 1.052). This circumstance plays just as large a role in the process of melting as does a breakdown of long-range order. In our case the spatial position of clusters is rigidly fixed by the zeolite framework, so that the position of the centers of gravity of clusters in the entire temperature range studied remains the same (long-range order of clusters, taken as a whole, is conserved). It is clear that the PT observed by us (curve 2) is based on the change in short-range order in clusters and on the orientation of clusters relative to the matrix. The main peak (curves 1 and 2) is most likely genetically related to melting.

The process of melting of such a small particle can be understood by analyzing the temperature dependence of the mean-square displacements of atoms from their equilibrium positions. As shown in Ref. 7, this quantity changes discontinuously at a certain temperature (T_m). (When a bulk specimen melts, this quantity causes a discontinuous change in volume and density.) An increase in the amplitude of vibrations of atoms, which increases the anharmonicity of the vibrations, changes the bond length, valence angle, and coordination number, and also decreases the lifetime of a cluster in a certain orientation relative to the matrix and increases the coefficient of self-diffusion of atoms inside a cluster (the coefficient or self-diffusion between clusters, which is determined by the activation barrier in 4-angstrom windows between zeolite cavities, in this case probably remains unchanged).

Thus, the observed PT are primarily related to changes occurring in an individual cluster located in a spatially ordered ensemble of strictly size-calibrated clusters and corresponds to what is called melting.

[1)]Since the volume of a cavity in zeolite (775 Å^3) is at least three times greater than the volume of a cluster (~240 Å^3), it may be assumed that the measurements were performed at constant pressure.

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