First-order phase transition in an approximately one-dimensional system

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The melting of mercury filaments with a diameter in the range between 20 Å and ~ 100 Å is investigated. As the filament diameter (d) is reduced, the phase-transition region shifts toward low temperatures (the transition shift amounts to $\sim 1/d$) and becomes diffuse over a large temperature interval (the diffuse region extends over a distance of $\sim 1/d^2$). The hysteresis that sets in between melting and solidification decreases and vanishes when $d \sim 20$ Å.

The size effects that arise in second-order phase transitions in dispersed metallic systems have been studied quite thoroughly. In particular, we have used previously extremely fine metallic filaments (i.e., those of an approximately one-dimensional system) to study the effect of fluctuations on a superconducting transition[1] and the dependence of the critical temperature of this transition on the filament diameter.[2] The first-order phase transitions in dispersed systems have been studied considerably less extensively. There have been virtually no experiments of this type performed using approximately one-dimensional systems as objects of investigation. The melting region of extremely fine mercury filaments can, on the other hand, be identified on the temperature curve of the resistance.[3] It is therefore of considerable interest to study this phase transition as a function of filament diameter, particularly since the study of this transition in terms of the resistance involves the use of a volumetric method. This letter is concerned with the study of this transition.

As in the previous experiments, the metallic filaments with a diameter in the range between 20 Å and ~ 100 Å were fabricated by injecting liquid metal (mercury, in our case) into the channels of natural chrysotile asbestos. The samples contained up to 10^6 ~ 1-cm-long parallel metallic filaments (the spacing between the adjacent filaments was 200–300 Å). The samples whose filaments had a small spread in diameter (not exceeding ~ 5%) were chosen for measurements. Figure 1 shows the resistance of these systems plotted as a function of temperature in the range between room temperature and ~ 100 K. The curves clearly show the melting region, which becomes gradually more diffuse and shifts toward low temperatures as the diameter is reduced. Also shown in Fig. 1 for comparison with bulk mercury is the $R(T)$ curve for mercury injected into an ~ 10-μm-diameter capillary (curve 5) held at a pressure of ~ 10 kbar (to prevent filament disconnection in the asbestos channels, we analyzed all the samples in self-contained chambers held at the same pressure). We see from the curves in Fig. 1 that the melting region extends over a large temperature interval, which is probably attributable to the fluctuations whose appreciable effect on the phase transitions in one-dimensional systems has been well established. At such a highly diffuse transition, it is not clear what point should here be regarded as the melting point. Since there are no physically sound criteria for determining this point on the $R(T)$ curve in

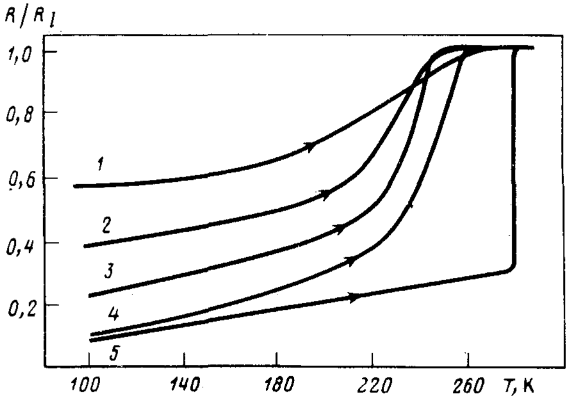

FIG. 1. Temperature dependence of the resistance of extremely fine mercury filaments with the following diameters: 1—d—20 Å; 2—25 Å; 3—35 Å; 4—45 Å; 5—a 10-μm capillary (the uniform pressure is ~10 kbar).

the melting region (although these criteria can be determined for second-order phase transitions in several cases[2]), we can arbitrarily assume that the melting point is that point at which the resistance changes only half as much as it does during melting. The dependence of a particular melting point on the diameter is shown in Fig. 2*a*. Also shown here is the region in which the transition becomes diffuse (dashed lines). The solid curve corresponds to the dependence $T = T_0(1 - d^*/d)$, where $d^* \sim 5.5$ Å and $T_0 \sim 280$ K, which is equal to the melting point of bulk mercury at a pressure of ~10 kbar. Curves of this type for the solidification point are shown in Fig. 3. We see from a comparison of these figures that a hysteresis sets in between melting and solidification. This hysteresis decreases, however, with decreasing filament diameter and vanishes at $d \sim 20$ Å. These results are in reasonable qualitative agreement with the melting and solidification points plotted as a function of the diameter for mercury islands[4] (we should note in this connection that Zhdanov[4] did not report any data on diffuse phase transitions).

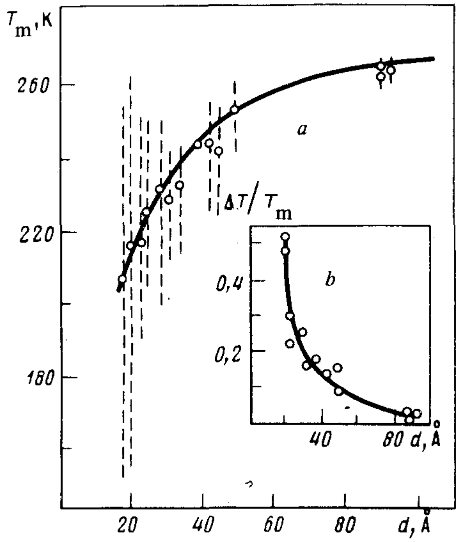

FIG. 2. (*a*) The melting point of extremely fine mercury filaments versus the diameter (dashed lines correspond to the diffuse-transition region); (*b*) the diffuse melting range versus the diameter.

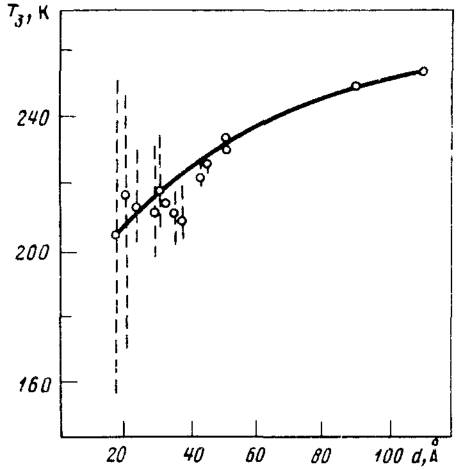

FIG. 3. The solidification temperature of extremely fine mercury filaments versus the diameter (dashed lines correspond to the diffuse-transition region).

Imry and Scalapino[5] discussed the theory of the effect of fluctuations on a first-order phase transition in the one-dimensional case. They concluded that fluctuations (just as a second-order phase transition) disrupt phase transitions in one-dimensional systems, although their effect is reduced considerably because of the heat of transition. A phase transition therefore occurs in a very narrow temperature interval; more precisely, this temperature interval increases exponentially with decreasing number of atoms in the filament cross section [i.e., $\Delta T \sim \exp(A/d^2)$, where ΔT is the diffuse-transition region). This conclusion seems to be inconsistent with our experimental result, since we have observed a rather broad transition whose diffuse region is inversely proportional to the number of atoms in the filament cross section [Fig. 2*b* is a plot of $\Delta T/T_m$ as a function of the diameter, and the solid curve corresponds to the relation $(\Delta T/T_m) = (D/d)^2$, where $D \sim 14$ Å].

The temperature fluctuations, whose effect on the diffuseness of a first-order phase transition was studied by Imry,[6] cannot explain the experimental data (the range of these fluctuations does not exceed 1 K in our case). The calculations carried out by Ping Cheng *et al.*[7] show that melting of clusters is accompanied by a markedly diffuse transition.

We note in conclusion that our data on diffuseness of melting and solidification show that a phase transition of this kind probably has a small correlation length. These data, along with the data showing that the melting point decreases appreciably, suggest that disorder in the arrangement of atoms increases (by an amount comparable to the atomic separation) on the surface of the filament as its diameter, which is determined by the curvature of the surface (a curved surface cannot have the same atomic packing as a bulk crystalline material), is reduced.

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