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Specific heat of amorphous Mo_xGe_{1-x} through the metal-insulator transition

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We have made absolute specific-heat measurements through the metal-insulator transition in thin-film Mo_xGe_{1-x}. We report results for γ and β and infer the thermodynamic electronic density of states. The density of states shows no critical behavior at the metal-insulator transition. There is also evidence of anomalous excess specific heat below the metal-insulator transition. We compare our results to current theories on localization and electron interactions.

In this paper we present results of specific-heat measurements performed on a thin-film amorphous system, Mo_xGe_{1-x}, through its metal-insulator transition. Transport measurements on related systems have continued the scaling theory result that there is no minimum metallic conductivity at the metal-insulator transition.[1-3] In addition, tunneling results[3,4] have confirmed the prediction that strong many-body effects cause $N(0)$, the single-particle tunneling density of states to approach 0 as the metal approaches the metal-insulator transition, and further that a correlation gap opens on the insulating side.[2-6] These results have been carefully reviewed.[7] Our experiments show that in accordance with Lee,[8] the thermodynamic density of states at the metal-insulator transition does not vanish, and, in fact, within the limits of our measurements varies smoothly with metal concentration over the entire range of composition.

We prepared the amorphous Mo-based alloy films by magnetron sputtering from targets of the respective elements in $\approx 6\times10^{-3}$-torr Ar gas at room temperature. The films averaged 1 μm thick, and were deposited on $6\times6\times0.2\text{-mm}^3$ sapphire substrates. The substrates were mounted on a rotating table with the targets aimed so as to impinge on a common area in order to achieve compositional homogeneity in the films. The rotation speed was typically 300 rpm and the sputtering rate was 5 Å/sec. This thin-film preparation technique has the advantage that we could not only compare our results directly to those obtained from tunneling on similar thin-film samples, but we could also prepare our samples extremely homogeneously down to microscopic length scales.[9]

We measured the specific heat of the samples by a time-constant-relaxation method, with τ ranging from 10 msec (at 1 K) to 1 sec (at 20 K), using silicon-on-sapphire sample platforms (bolometers).[10] The absolute accuracy of the total heat capacity of the sample plus the addenda, as confirmed by measurements on known standards, is 1% in the temperature region where we take our data.

Since the contribution of the sapphire, aluminum contact pads, and the electrical lead wires to the total heat capacity ranges from 75% of the total (at ~10 K) to 85% of the total (at ~2 K), we are limited to a sample specific-heat accuracy of 4–7%. The renormalized density of states (γ^*), and Debye temperature (Θ_D), are obtained using a fit to $C/T=\gamma^*+\beta T^2$ above T_c, coupled with the constraint that the entropy be the same in the superconducting state and the normal state. Thus, the values of γ^* and Θ_D are measured with an accuracy of ± 5%.

Figures 1 and 2 show the actual specific-heat data, plotted as C/T vs T^2, for our samples in this study. We have presented the raw data here, because it makes visually clear the points that we will address in more detail later. The following occur with decreasing metal concentration: the suppression of T_c (Ref. 1) and γ^*, the increase in slope and the appearance of curvature in the data.

In Fig. 3, we have plotted the extracted values of γ^*, the electronic coefficient of specific heat. Mo_xGe_{1-x} can only be prepared in the amorphous state from $x=0$ to $x=0.8$; for $x\geq0.8$ it forms a bcc lattice. However, amorphous Mo can be made by nitrogen stabilization,[11,12] and we have included the value of γ^* from this reference to show the value that we would expect to see at the highest Mo concentration. It is particularly worthy of note that γ^* varies linearly with the concentration of molybdenum, as expected of any local density of states model.

Finally, Fig. 4 shows the values of the Debye temperature, Θ_D, calculated from the slope (at $T=0$) of the data in Figs. 1 and 2. Again, we have included results from literature, to show the values at the extremes of metal concentration.

If we look at these figures as a group, the most striking feature is that the thermodynamic properties of the system change smoothly and monotonically as a function of metal concentration over the entire amorphous range. There is no evidence of any discontinuity or phase transition. This is especially unusual in light of the various electrical transitions (from superconductor to metal to insulator)[1] which the system undergoes.

In what follows, we focus on the most intriguing figure, Fig. 3. In the metallic region of the phase diagram, it is quite reasonable to see a finite γ^* proportional to [Mo]. But how can we explain the fact that this behavior seems to continue through the metal-insulator transition?

There is no evidence for any amorphous phase separation on a microscopic scale.[13] According to the structural model by Kortright, Mo atoms actively modify a random tetrahedral network of Ge atoms near the metal-insulator transition, resulting in a uniform distribution of two types of structure, a Mo-modified amorphous structure and a Ge random tetrahedral network on a very fine (< 40 Å) scale. We suggest such a structure could show a finite γ^*, and that, in fact, the metal atoms do not actually have to

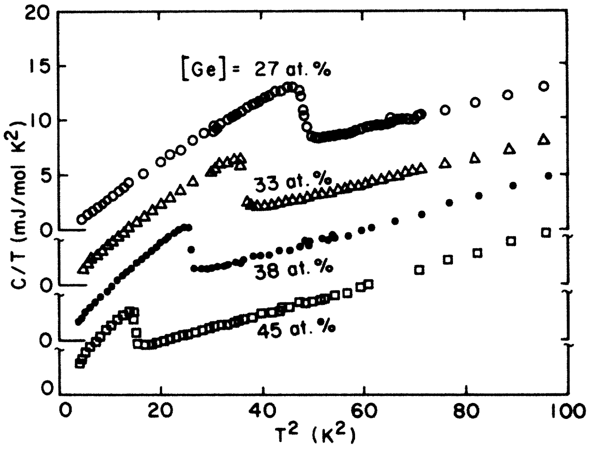

FIG. 1. Specific heat of Mo_xGe_{1-x} alloys in the metal-rich region.

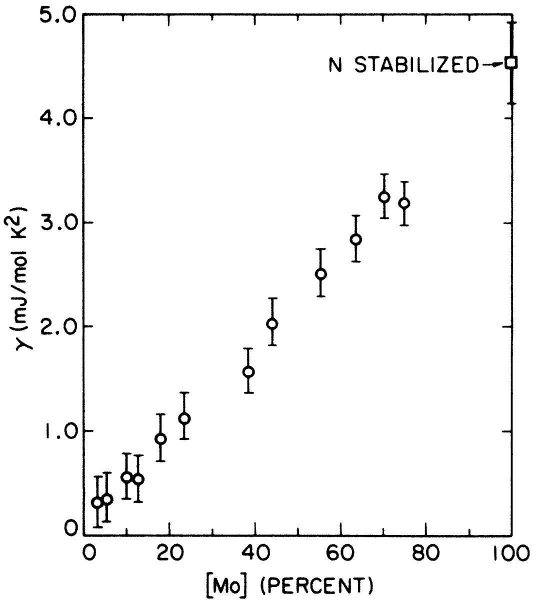

FIG. 3. Values of γ^*, electronic specific-heat coefficient, for this study.

be in contact with each other to produce a "metallic" or linear term in the specific heat. A linear term in the heat capacity of an amorphous metal is known to result from either an ensemble of electrons with access to a continuum of states near the chemical potential, μ, or a distribution of two level states. Estimates of the magnitude of the contribution in the latter case are much too small to account for the measured magnitudes. In the former case, for N atoms in the ensemble, the spacing of the energy levels will be $\sim E/N$, with $E \sim 4.5$ eV, the energy width of the molybdenum d band.[14] When this spacing becomes $\leq k_BT$, the ensemble will begin to show a continuum of states near ε_F. At $T = 1$ K (the limit of our measurement), this occurs at $N \approx 10^4$. So, if one electron could sample N atoms, where $N \geq 10^4$ then the electron would statistically see many other electron states within k_BT of its energy μ thus giving a linear γ^*. This then is not a question of whether the sample is a metal or an insulator at all, but rather, how far an electron can move during the time period of our measurement (≥ 10 msec at the lowest temperatures).

On the metallic side of the metal-insulator transition, the electron motion is governed by diffusion, and, in fact, on these time scales, the diffusion constant is large enough by [Mo] = 11% that the electron can diffuse over 1000 Å.

However, on the insulating side of the metal-insulator transition, at finite temperature, the electron has been shown to move by variable range hopping.[1] To see how many Mo atoms it can be expected to have interacted with

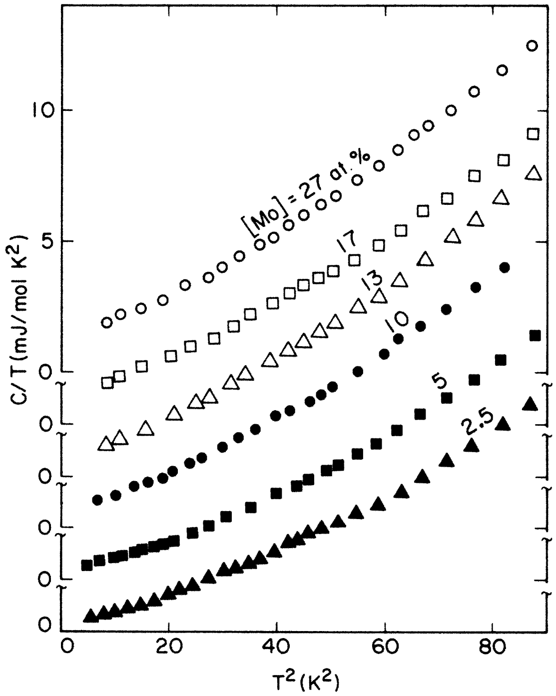

FIG. 2. Specific heat of Mo_xGe_{1-x} alloys in the metal-poor region.

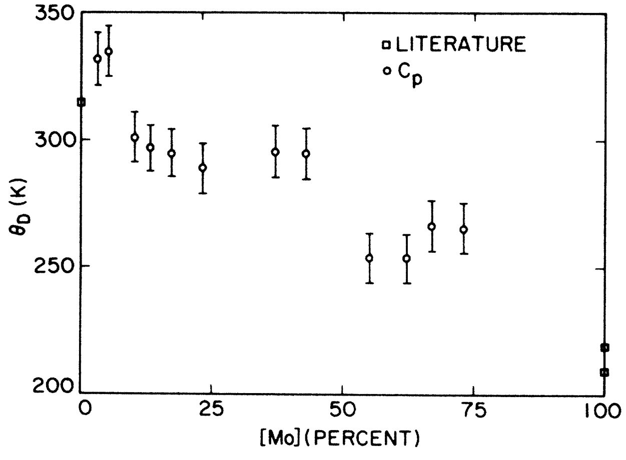

FIG. 4. Values of Θ_D, Debye temperature, for this study.

on a 10-msec time scale, we must calculate the hopping distance, and the hopping probability. From the theory of variable range hopping,[15] we have that the hopping probability per unit time, $1/\tau$, is given by

$$1/\tau = \nu_{\text{ph}} \exp(-2\alpha\bar{R} - W/k_BT) \ .$$

Here, $\bar{R}$ is the average hopping distance, and $\alpha = 1/\xi$. Thus, using these results,[15] at $T = 1$ K, the hopping attempt frequency would be $\nu = k_BT/h \approx 10^{12}$ and the expected number of Mo atoms sampled would be $N \approx \nu(1/\tau)\bar{R}^3[\text{Mo}]$ (where [Mo]≡concentration). At [Mo] =9%, we find $\bar{R}$ to be 44 Å, and the hopping rate to be $\sim 10^6$ and so the expected distance traveled by the electron in 10 msec would be about 440 Å giving $N \approx 10^6$. By 5%, $\bar{R}$ has increased to 65 Å, but the hopping rate has dropped to $\sim 10^3$, and so the expected travel is correspondingly decreased to about 80 Å giving $N \approx 10^4$. This puts us just at the limit of our prediction, and this is, in fact, the point where it becomes difficult to determine whether γ^* is, in fact, still finite.

However, these ideas do predict that as we go down in temperature, we should see a downturn in the specific heat at Mo concentrations of 5–7% at 0.5 K. We are currently modifying our apparatus to investigate this region.

Finally, we discovered that as the concentration of Ge increased, that if we attempted to fit our data to a simple polynomial expression, not only did we have a growing αT^5 term, but there was also an excess specific heat that could not be expressed by a polynomial, and which increased as [Mo] decreased. That is, we used a least-squares method to fit our data, and the residual specific heat was that which remained when we subtracted the fit from our data. In all cases, this excess had vanished by 10 K, and was so small that we show only the total integrated value, $\bar{C} = \int_0^{10\text{K}} C\, dT$. This integrated excess specific heat is plotted in Fig. 5. These data are interesting because Altshuler and Aronov's theory[16] predicts nonpolynomial terms in the specific heat that should increase with decreasing metal concentration. However, for our materials this theory falls far short of the values we found. Further, the excess specific heat is found on the insulating side of the transition, which is not predicted. On the other hand, Pohl[17] noted that there is excess specific heat present in 100% amorphous Ge above 10 K, with an integrated value over an order of magnitude higher than our results. Finally, we note that other research on amorphous materials has also found a term in the specific heat proportional to T^5 in amorphous materials[18,19] but as yet there is no adequate explanation for this term. Clearly, this problem needs further research.

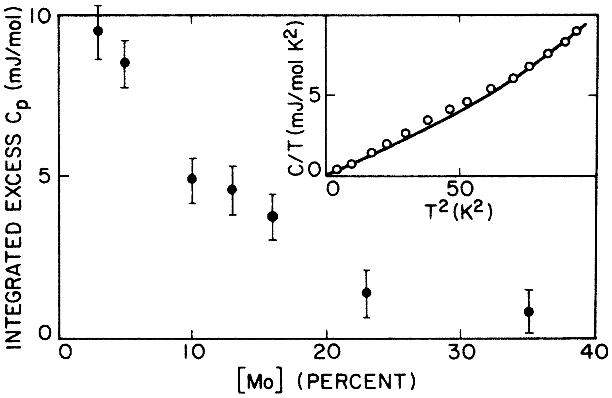

FIG. 5. Total integrated excess specific heat in the metal-poor region.

In conclusion, these measurements represent the first to study the specific heat of a thin-film metastable amorphous-alloy system through its metal-insulator transition. Our results show that the thermodynamic density of states decreases continuously with decreasing metal concentration, and does not become zero at the transition, which we have shown to be consistent with Mott's variable range hopping conduction model. In addition, we found that our samples show excess specific heat near the transition, which suggests that there are additional degrees of freedom to be considered. This research is currently continuing in magnetic fields.

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