Superconductivity near the metal-insulator transition in amorphous α-$Ge_{33}As_{12}Se_{55}$

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Experiments have been carried out on the effect of pressures P up to 220 kbar on the electrical resistance of the amorphous alloy α-$Ge_{33}As_{12}Se_{55}$ over the temperature range 1.4–300 K. Near the metal-insulator transition ($P \approx 160$ kbar), superconductivity sets in with a critical temperature T_c which increases rapidly to $T_c = 3.5$ K as P is raised to 200 kbar. The effect is reversible if P does not exceed 200 kbar.

The effect of localized Fermi electrons on superconductivity in systems with disorder has recently become the subject of a lively discussion.[1–4] Of particular interest is the behavior of such a system near the metal-insulator transition (the Anderson transition) as the Fermi level E_F crosses the mobility threshold E_c. The theoretical predictions are compared with experiment primarily on the basis of data on the decrease of T_c in high-temperature superconductors upon an increase in the disorder as a result of irradiating the samples.[5]

New possibilities for studying the nature of the superconductivity in amorphous materials come from experiments under high pressures, which make it possible to monotonically vary the relative positions of the levels E_F and E_c. Suitable materials for studies of this sort are the amorphous chalcogenides. Experiments at high pressures have shown[6,7] that for the amorphous chalcogenides α-As_2S_3, α-As_2Se_3, α-As_2Te_3, and α-$Ge_{16}As_{35}Te_{23}S_{21}$ the electrical resistance R at room temperature decreases smoothly with increasing pressure, and in α-As_2S_3 and α-As_2Se_3 the optical gap E_g shows the same behavior. In addition, the temperature dependence of R for α-As_2Se_3 and α-As_2Te_3 has been measured over the intervals 77–300 K and 0–100 kbar. The equality of twice the activation energy E_a to the optical gap E_g in α-As_2Se_3 indicates that the Fermi level lies at the center of an "energy gap." in α-As_2Te_3, E_a decreases smoothly with the pressure, vanishing at $P \approx 100$ kbar (Ref. 7). At approximately the same pressure the sample goes superconducting with $T_c \approx 4.4$ K. X-ray studies[7] of an α-As_2Te_3 sample have shown that over the entire pressure interval, and after the transition to a metallic state, the short-range order is preserved; i.e., the appearance of superconductivity is not related to a polymorphic transformation.

However, since the T dependence of R in α-As_2Te_3 has been measured at temperatures above 77 K, and the superconductivity has been detected at only one pressure, we cannot draw conclusions of any sort about the behavior of T_c upon the transition to a metallic state under pressure on the basis of these results.

In the present letter we report a study of the behavior $R(T, P)$ over the tempera-

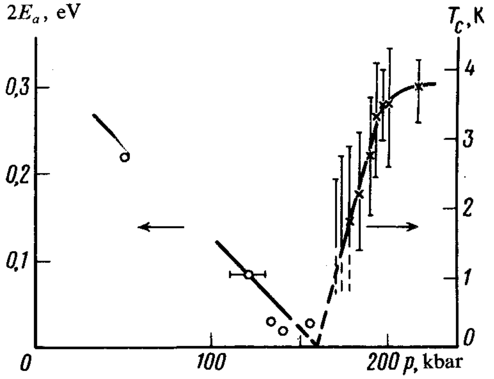

FIG. 1. Pressure dependence of $2E_a$ (scale at the left) and T_c (scale at the right). Horizontal error bar—Error in the determination of the pressure; vertical error bar—width of the superconducting transition (a dashed line indicates that the transition is not completed). T_c is determined from the center of the transition.

ture interval 1.4–300 K at pressures up to 220 kbar in the amorphous chalcogenide α-$Ge_{33}As_{12}Se_{55}$.

The pressure is imposed by an anvil of polycrystalline diamonds by the method of Ref. 8. The resistance is measured by a four-contact method. Several measurements are taken from the same sample as the pressure is progressively raised and lowered, so that it is possible to achieve a high accuracy in the determination of the relative change in the pressure and in the resistivity ρ; it also becomes possible to study the reversibility of the observed effects.

The results show that during the compression of α-$Ge_{33}As_{22}Se_{55}$ at $T = 300$ K the resistivity ρ falls off smoothly from $\sim 10^3$ Ω·cm at $P = 0$ to 0.3×10^{-3} Ω·cm at $P = 220$ kbar. There is a corresponding change in the temperature dependence $R(T)$. At $P < 130$ kbar, the T dependence of R is the typical dependence of a disordered semiconductor. Parts of the $R(T)$ curves on which an exponential change in R is observed can be clearly detected at least up to 130 kbar, so that it becomes possible to reliably determine the changes in the activation energy E_a at these pressures. Figure 1 shows the P dependence of $2E_a$ (the curve at the left) as calculated from the slope of the $\ln R(1/T)$ curves. The activation energy decreases upon compression and extrapolates to zero at $P \approx 160$ kbar.

At higher pressures, the $R(T)$ curves retain their poorly defined semiconductor nature; the increase in R with decreasing temperature becomes smaller with increasing pressure. However, even at $P = 170$ kbar we see a sharp decrease in the resistance at low temperatures on the $R(T)$ curves; at higher pressures, this decrease converts into a clearly detectable superconducting transition (Fig. 2).

The most interesting and unusual (for the crystalline state of a nontransition material) aspect of the onset of the superconductivity is the strong dependence of T_c on the applied pressure (the curve at the right in Fig. 1): In the pressure interval 170–195 kbar, the derivative dT_c/dp is ~ 0.1 K/kbar, while at pressures above 195 kbar the transition temperature T_c changes much more slowly.

The P dependence of T_c is reversible if P does not exceed 200 kbar. When the limiting pressure does exceed 200 kbar, a hysteresis is seen on the $T_c(P)$ curve, and a

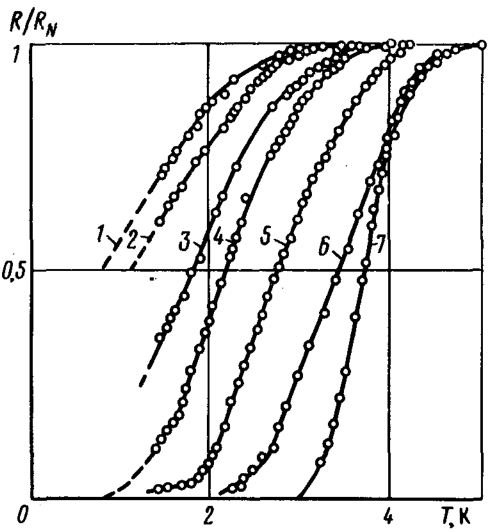

FIG. 2. Superconducting transitions in α-$Ge_{33}As_{12}Se_{55}$ at various pressures (R_N is the resistance at the beginning of the transition): 1—170 kbar; 2—173 kbar; 3—178 kbar; 4—183 kbar; 5—190 kbar; 6—200 kbar; 7—218 kbar.

more obvious hysteresis is seen on the $E_a(P)$ curve, implying the onset of irreversible structural changes in the sample. By analogy with amorphous α-As_2Te_3, it may be suggested that α-$Ge_{33}As_{12}Se_{55}$ crystallizes at $P \gtrsim 200$ kbar and that an impurity of a crystalline phase is preserved in the samples as the pressure is lowered.

These results on the P dependence of T_c seem to indicate that the superconductivity sets in at a metal-insulator transition in the immediate vicinity of the point at which E_a vanishes, i.e., when the Fermi level intersects the mobility threshold. The onset of superconductivity at $E_F \approx E_c$ and the increase in T_c as E_F moves away from the mobility threshold are in general agreement with the results of Refs. 1–4, where a decrease in T_c as E_F approached E_c from the metallic side of the metal-insulator transition was linked with an increase in the effective Coulomb repulsion.

An alternative explanation for the appearance of superconductivity in this system based on the precipitation of distinct superconducting clusters upon compression sounds unconvincing, since the values of T_c and the P dependence of T_c for the known high-pressure crystalline phases of the elements making up α-GeAsSe, and possibly their compounds, do not agree with the results of the present study.

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