Low-temperature anomalies in the magnetoelectric properties of amorphous gallium antimonide

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Anomalies have been found in the electrical and magnetic properties of a mixture of amorphous and crystalline phases of gallium antimonide at low temperatures. These anomalies apparently stem from a superconductivity of an exciton nature. The superconducting features can be traced up to $T \sim 100$ K.

1. Composites consisting of a metal and an insulator[1] or of a metal and a semiconductor[2] have long been regarded as promising systems for observing a high-temperature superconductivity. It has been shown[3] for a tunneling mechanism of exciton superconductivity[2] that the appearance of superconducting properties could be expected in mixtures of an amorphous semiconductor phase and a crystalline phase (it was assumed that the amorphous semiconductor might play the role of the metal in this case). The standard expressions

$$T_c \approx \Delta E \exp(-1/g), \tag{1}$$

$$g = \lambda_{ex} - \mu^* \tag{2}$$

for a semiconductor with $E_g \sim 1$ eV and $\omega_p \sim 10$ eV were used in Ref. 3 to derive the estimate $T_c = 70$–500 K. Since the constant $\lambda_{\rm ex}$ depends on the relation between the depth to which the wave function penetrates into the insulator, D, and the size of the superconducting regions, L,

$$\lambda_{ex} \sim (1 + L/D)^{-1}, \tag{3}$$

the condition $g > 0$ imposes an upper limit on the size of the superconducting particles: $L \lesssim L_m \sim 60$ Å (Ref. 3). On the experimental side, there has been essentially no study of superconductivity in semiconductor systems of this sort. In the present letter we report a study of this question.

2. For the study we selected bulk samples of the system consisting of amorphous and crystalline gallium antimonide, $(a\text{-GaSb})_x(c\text{-GaSb})_{1-x}$, synthesized by quenching a melt under high pressure.[4] A change in the concentration of the amorphous phase from $x = 0$ to $x = 1$ results in a pronounced growth of the resistivity of the samples and induces a metal-insulator transition at $x = x_c \sim 0.4$ (Ref. 4). In contrast with Ref. 3, the degenerate crystalline semiconductor with a quasimetallic conductivity in our case should therefore be identified as the "metal," and the high-resistivity *a*-GaSb as the "insulator" (at low temperatures, the conductivities of samples with $x = 0$ and $x = 1$ differ by a factor of 10^9; Ref. 4). With increasing x, there is a decrease in the length scale of the regions of the crystalline phase; it becomes a simpler matter

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to satisfy the condition $L < L_m$; and, according to (1)–(3), the superconducting properties of the system may be amplified. The method for determining x is described in Ref. 4.

For the electrical measurements, we attached ohmic contacts to the samples. To improve the reliability of the measurements, we used several methods: soldering with a low-melting solder; electrolytic deposition of copper, followed by a soldering of conductors in place; and the attachment of thin silver-plated wires by electric-arc welding. The temperature and field dependences of the electrical conductivity of these samples found in our measurements did not depend on the particular method used to fabricate the contacts.

3. On the curves of $\rho(T)$ for the samples with $x \sim 0.3 < x_c$ we see a change in slope at $T = T_c \lesssim 10$ K, which can be completely suppressed by imposing a magnetic field $H \sim 120$ kOe (Fig. 1). This fact, combined with the measurements of the magnetic moment (all the samples turned out to be diamagnetic), indicates, in our opinion, that the system $(a\text{-GaSb})_x(c\text{-GaSb})_{1-x}$ exhibits superconducting properties. The finite resistance of the sample at $T < T_c$ means that there is no flow through a superconducting phase (Fig. 1) and that the superconductivity and the positive magnetoresistance at low temperatures stem from isolated clusters. The reason why the transition is stretched out along the temperature scale (Fig. 1) is a dispersion of the superconducting properties.

The mixture of amorphous and crystalline phases studied in the present experiments was stable at temperatures $T \lesssim 340$ K, and the curves of $\rho(T)$ in this temperature interval are completely reversible upon repeated temperature-scanning cycles. When the samples are heated above 340 K, a crystallization of the amorphous phase begins ($x \to 0$), accompanied by an irreversible decrease in ρ. As a result of this process, there is also a change in T_c which corresponds to the reversible part of the $\rho(T)$

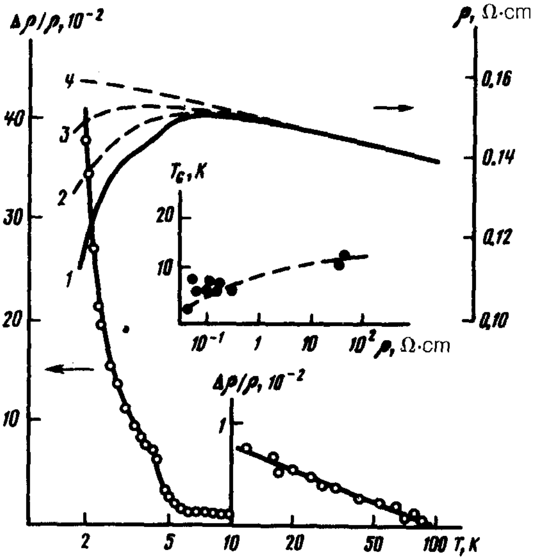

FIG. 1. Temperature dependence of the resistivity in various magnetic fields. 1—0 kOe; 2—20; 3—40; 4—120 kOe. Temperature dependence of the magnetoresistance in a 120-kOe field for a sample with $x \sim 0.3$.

curve: The temperature of the slope change initially decreases, and when $x = 0$ is reached, the superconducting features disappear (the maximum annealing temperature did not exceed 370 K).

There is a tendency for T_c to grow with increasing degree of disorder, of which we can take $\rho(T_c)$ as a measure (see the inset in Fig. 1). This behavior contradicts the theoretical arguments of Ref. 5, according to which T_c should decrease as $x \to x_c$ because of a growth of the Coulomb parameter μ^* due to a degradation of the screening. According to the model outlined in §1, in the presence of a dispersion in L there would be, at a fixed value of T, a maximum size $L(T)$ of such a nature that clusters with $L < L(T)$ are in a superconducting state, while those with $L > L(T)$ are in a normal state. As the temperature is lowered, there is a scanning over the dimensions of the superconducting regions [$L(T)$ increases, reaching L_m in the limit $T \to 0$], and for this reason the transition is stretched out. During annealing, the size of the crystalline regions increases; this effect reduces T_c, according to (1)–(3). The growth of T_c with the disorder can be explained in a similar way, since the cluster size L decreases with increasing x and ρ (Ref. 4). The superconducting properties of the *a*-GaSb can thus be explained in a natural way in this model.

Interestingly, the positive magnetoresistance, which increases sharply at $T \lesssim T_c$, does not vanish at $T = T_c$. It instead has an extended decay region, and only at $T \gg 100$ K do we find $\Delta\rho/\rho \approx 0$ within the experimental error (Fig. 1). At $T \lesssim 77$ K and $H \lesssim 150$ kOe, the Hall mobility μ does not depend on the magnetic field and has a value ~ 0.5 cm^2/(V·s). We can thus estimate the Lorentzian component of the positive magnetoresistance: $\Delta\rho/\rho \sim 0.5(\mu \cdot H)^2 \sim 2 \times 10^{-7}$ for $H = 120$ kOe (in the field range under consideration here, there are no indications of a magnetic freezing or of the presence of two groups of carriers on the field dependences of the positive magnetoresistance and the Hall voltage). If we assume that $(a\text{-GaSb})_x(c\text{-GaSb})_{1-x}$ has regions with a dimension $L < L(T_c \sim 10$ K), we might be able to link the extended decay region of the positive magnetoresistance with the onset of a high-temperature exciton superconductivity,[1-3] while the relatively low value of the positive magnetoresistance might be due to a low concentration of small clusters. The validity of this suggestion could be tested on samples containing a high concentration of the amorphous phase, where the fraction of the small particles of the crystalline phase should increase, and the relative amplitude of the positive magnetoresistance should also increase at high temperatures.

4. In the concentration interval $x \sim 0.7 > x_c$, the test samples are characterized by an activation temperature dependence $\rho(T)$, against the background of which we observe, at $T \approx 63$ K, a structural feature accompanied by a pronounced positive magnetoresistance (Fig. 2). This effect cannot be attributed to an ordinary hopping conductivity, since in this case the positive magnetoresistance at $H =$ const is described by a smooth function in the coordinates[6] $\Delta\rho/\rho = f(T)$, while experimentally we observe a complex, nonmonotonic dependence (Fig. 3). The quantity $\Delta\rho = \rho(H) - \rho(0)$ has a much simpler behavior as a function of the temperature (Fig. 2): At $T > 63$ K, $\Delta\rho$ is small and remains essentially constant over the temperature. At $T = 63$ K, the positive magnetoresistance increases sharply, reaching saturation at $T \sim 15$ K. At $T \lesssim 5$ K we observe a second growth region. The complex shape of the $\Delta\rho/\rho$ curve (Fig. 3) results

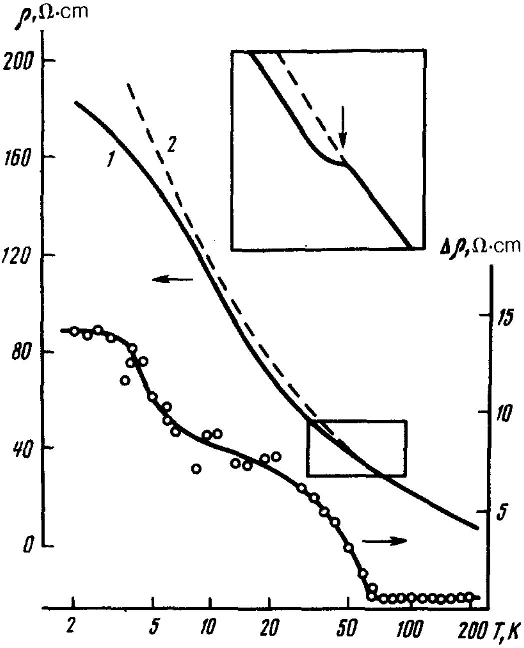

FIG. 2. Data on $\rho(T)$ and $\Delta\rho(T)$ for a sample with $x\sim0.7$. The boxed part of the $\rho(T)$ curve is shown in larger scale in the inset. 1—0 kOe, 2—120 kOe.

from the division of $\Delta\rho(T)$ by $\rho(T)$ (Fig. 2). The low-temperature feature in $\Delta\rho(T)$ lies at $T\sim T_c$ in the low-resistance samples (Fig. 1) and is apparently a consequence of a superconductivity of clusters which are of the same size as in the case $x\sim0.3$. The amplitude of the positive magnetoresistance in the region $10\text{ K}\lesssim T\lesssim60\text{ K}$, divided by the value of the positive magnetoresistance at $T\lesssim10$ K for the sample with $x\sim0.7$, is

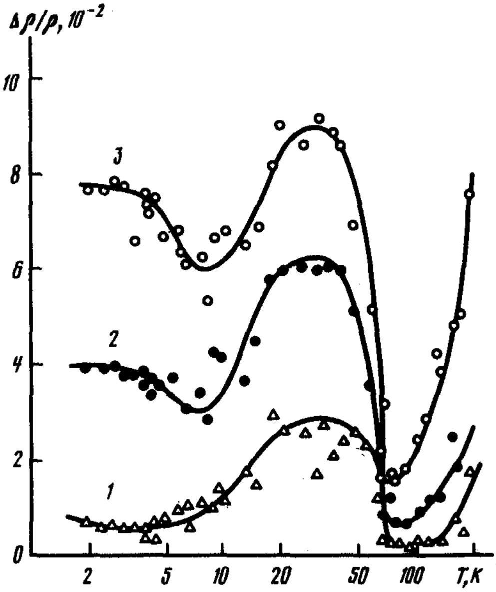

FIG. 3. Magnetoresistance of a sample with $x\sim0.7$. 1—40 kOe; 2—80; 3—120 kOe.

large in comparison with that in the case $x \sim 0.3$ (Figs. 1 and 2), as it should be in our model. Furthermore, the temperature at which the growth of the positive magnetoresistance begins (63 K at $H = 120$ kOe) shifts up the temperature scale with decreasing H.

As an additional argument in favor of the existence of a high-temperature superconductivity in the $(a\text{-GaSb})_x(c\text{-GaSb})_{1-x}$ system, we might cite the presence of a hysteresis on the $\rho(H)$ curves at $T \lesssim 100$ K for $x \sim 0.3$ and at $T \lesssim 60$–70 K for $x \sim 0.7$. This hysteresis is probably due to a capture of flux in a type-II superconductor. A final resolution of the nature of the high-temperature anomalies will have to await a detailed study of the magnetic properties, which is the subject of a separate study.

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