

# Metal-insulator transition during the order-disorder transition of a metastable phase in the Zn-Sb system

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Analysis of the electrical characteristics of a  $\text{Zn}_{43}\text{Sb}_{57}$  sample shows that the order-disorder transition of the metastable crystalline phase during heating occurs initially along grain boundaries. As a result, a granular metal forms.

Heat and pressure treatment of alloys of the Zn-Sb system gives rise to a new intermediate phase ( $\delta$ ) with a composition with  $\approx 60$  at. % Sb, which, through quenching under pressure, can be produced in a metastable state at atmospheric pressure and liquid-nitrogen temperature. This crystalline phase has an orthorhombically distorted hexagonal structure. At  $T_c = 6.6-6.8$  K it goes superconducting.<sup>1,2</sup> A heating restores the sample to an equilibrium crystalline state ( $\text{ZnSb} + \text{Sb}$ ) through an intermediate amorphous state; the spontaneous disordering of the  $\delta$  phase is observed at temperatures below room temperature, and the final crystallization of the amorphous phase is observed at temperatures above 150 °C. A disordering of metastable phases is also observed several other binary systems.<sup>2-5</sup>

The amorphous intermediate ( $\alpha$ ) phase of Zn-Sb has a conductivity of a semiconducting nature. It is thus possible, by means of a slow and carefully controlled heating over the temperature interval 77-300 K, to gradually bring the sample from a metallic state to a semiconducting state. We have undertaken a study of the electrical properties of a sample changing in this matter, using x-ray analysis to monitor its structural state.

An alloy of the composition  $\text{Zn}_{43}\text{Sb}_{57}$  was synthesized by melting elements of 99.999% purity in evacuated quartz cells. The heat and pressure treatment of the samples was carried out in a quasihydrostatic pressure chamber at  $P = 90$  kbar and  $T = 350$  °C for 2 h. At this point the temperature of the sample was reduced sharply (at  $\sim 50$  deg/s to  $T = 50$  °C) to liquid-nitrogen temperature, and then the pressure was reduced to atmospheric. For the electrical measurements we used samples with a  $1.6 \times 1.8\text{-mm}^2$  rectangular cross section and a length of 7 mm. The resistance of a sample was measured by a four-contact method (with clamp-on contacts of gold wire) at a current frequency of 34 Hz. The holder with the sample was placed in a cryostat in which the temperature could be varied from 1.2 K to 300 K.

Another sample, a "witness," of the same composition, was placed beside the sample used for the measurement of the electrical resistance and subjected to the same heat treatment. An x-ray diffraction analysis of the witness sample was carried out in a low-temperature attachment to a diffractometer at  $T = 100$  K by a "photographic method" with  $\text{CuK}\alpha$  radiation. The amount of  $\delta$  phase was estimated from the change

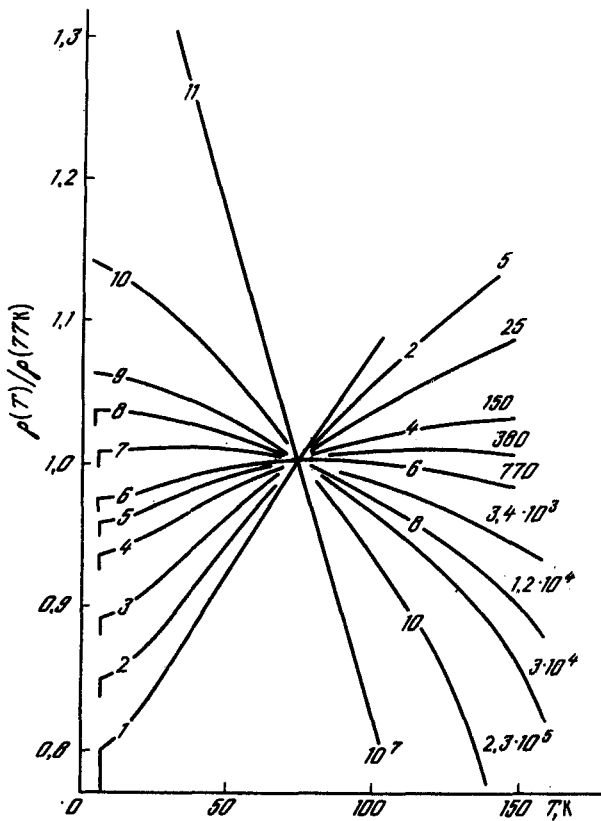


FIG. 1. Temperature dependence of the electrical resistivity of a sample in various stages of disordering. The curve labels at the right are the ratios  $R/R_0$  of the resistance at  $T=77$  K in the current state to that in the initial state of the sample.

in the intensity of the lines of this phase; the intensity of a nickel powder was used as a reference.

In both methods, the samples were mounted in the holders at liquid-nitrogen temperature.

Line 1 in Fig. 1 shows the temperature dependence of the resistivity,  $\rho_\delta(T)$ , of an initial  $\delta$ -phase sample (the absolute value of the resistivity at 77 K was about  $50 \mu\Omega \cdot \text{cm}$ ). The  $\rho_\delta(T)$  curve is reproducible within  $10^{-4}$  during repeated cycling from a temperature of 2 K to 105 K (the curve at the right in Fig. 2 shows the superconducting transition in larger scale). If we go beyond the reversible interval, we find an irreversible increase in the resistivity, which depends on both the time and the temperature. For example, for a transition to curve 2 it is necessary to heat the sample to 120 K for 5 min. After a given controlled heating, the sample is rapidly cooled to liquid-nitrogen temperature and prepared for the next measurement cycle. The interval of reversible changes in the resistivity becomes progressively wider, increasing initially rapidly and then more slowly, to 165 K on curve 11.

Curves 1-4 demonstrate the metallic behavior of the resistivity over the entire temperature interval. An increase in the resistivity by a factor of 100 is accompanied

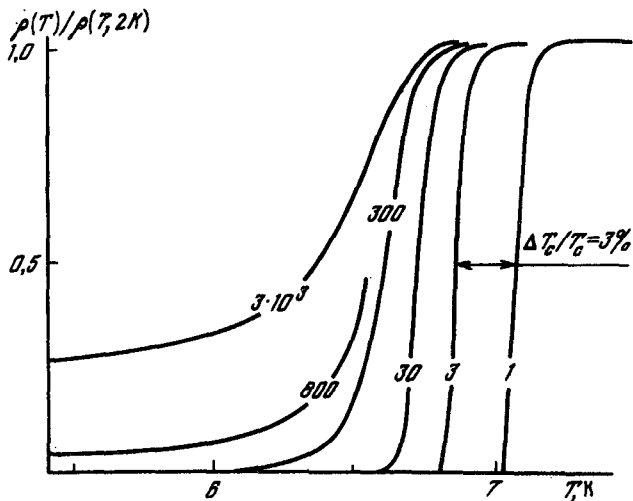


FIG. 2. Superconducting transition in various stages of disordering. The curves are labeled with the resistance ratio  $R/R_0$ .

by a decrease of only 5–6% in the critical temperature  $T_c$ . The  $\rho(T)$  curve then acquires a maximum, which gradually shifts down the temperature scale (curves 5–8). The beginning of the superconducting transition stops shifting along the temperature scale, but the transition initially becomes broader and then incomplete: The resistivity does not drop to zero (Fig. 2). Along curves 9–11 we then have  $\partial\rho/\partial T < 0$  everywhere. It is important to note that curve 11 by no means corresponds to the last stage of the disordering of the sample: It follows from the x-ray measurements that about 50% of the sample is still in the metallic phase.

From the experimental data we can draw certain conclusions regarding the nature of the disordering process in its initial stages. If the sample remained microscopically homogeneous in the course of the heat treatment, and if the number of free carriers decreased as a result of their arrival at deep capture centers and the formation of randomly directed covalent bonds in the metallic lattice, the increase in the resistivity would have unavoidably been accompanied by significant changes in  $T_c$ . Further evidence against homogeneity is the fact that the half-width of the lines of the  $\delta$  phase on the Debye patterns does not change during the initial stages of the disordering.

Also at odds with the experimental data is the “opposite-limit” model in which the growth of the  $a$  phase occurs from random, chaotically arranged nucleating centers. In this case, according to percolation theory,<sup>6</sup> a transition to an insulating  $a$  state should occur at a threshold value of the fraction of the  $\delta$  phase,  $x_c = 0.15$ – $0.20$ , and the proximity to the threshold could be determined from the relative increase in the resistivity  $\rho$  from the initial value  $\rho_\delta$  as a function of the fraction of the  $\delta$  phase,  $x$ . Using the expression for  $\rho(x)$  near the percolation threshold,

$$\rho(x) / \rho_\delta \approx 0.3 (x - x_c)^{-1.6} ,$$

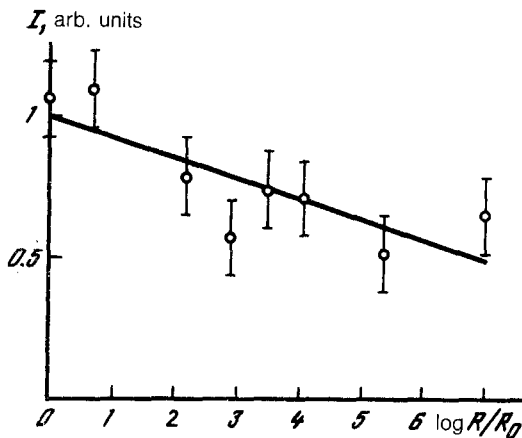


FIG. 3. Changes in the integrated intensity of the lines of the  $\delta$  phase ( $d = 1.877 \text{ \AA}$ ; Ref. 2) in the initial stages of disordering.

we find that in this model the distance to the threshold,  $x - x_c$ , is 0.07, 0.02, 0.01, and 0.007 for curves 3–6, respectively. It seems unlikely that a comparatively straightforward heat treatment would make it possible to controllably change the state so close to the threshold. Furthermore, the data in Fig. 3 indicate that the amount of the initial  $\delta$  phase in these states of the sample is vastly greater than  $x_c$ .

The experimental results can be explained under the assumption that the  $a$  phase arises and grows along the boundaries of crystal grains, gradually forming a thin film around them. If the average grain size is  $d$ , and if the average thickness of the film of the  $a$  phase is  $s \ll d$ , then the volume fraction of the  $a$  phase at the point at which the film covered all the boundaries would be only  $s/d$ . The progressive increase in the resistivity in series of states 1–11 in Fig. 1 can be explained in a very natural way on the basis of this model of a thickening of the film. Judging from the width of the lines on the Debye pattern,  $d$  is no less than  $500 \text{ \AA}$ . We can draw conclusions about the scale of  $s$  from the circumstance that at  $R/R_0 = 800$  a residual resistivity appears below the superconducting transition: A tunneling of the superconducting pairs can no longer combine all the metal grains into a single superconducting cluster ( $s \approx 30\text{--}50 \text{ \AA}$ ). A one-particle tunneling still leads to a metallic conductivity,  $\partial\rho/\partial T > 0$ , both at  $T > T_c$  (curves 6 and 7) and at  $T < T_c$ .

Granular metals have been the subject of active research for a long time now.<sup>7–10</sup> The entity which has been observed in these experiments has several distinctive features. It has been synthesized by a method fundamentally different from the usual method: by a thermally stimulated decomposition of a metastable phase, rather than through the deposition of a film. All of the states, from metallic to insulating, play out in succession in a single sample. Because of the correlated distribution of the insulating phase, the rupture of the infinite metallic cluster occurs when the fraction of the metallic phase in it is  $x \gg 0.15$ . The conductivity remains of a metallic nature at low temperatures in the region where the resistivity is controlled by tunneling processes. The range of the resistivity on the metallic side of the transition is nearly four orders of magnitude at a fixed temperature.

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