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Semiconductor-superconductor transition in granular Al-Ge

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The electrical resistance of granular Al-Ge specimens has been measured for various metal concentrations around the metal-insulator transition. We find that, in a narrow range of metal concentrations, the system is semiconducting in the normal state and yet undergoes a superconducting transition. It is shown that the occurrence of the semiconductor-superconductor transition is governed by the interplay between the intergrain tunneling coupling energy, the Josephson coupling energy, and the Coulomb charging energy, and is possible only for granular systems with large enough grains.

The possible occurrence of a semiconductor-superconductor transition in granular materials was discussed recently by several authors.[1–5] We have found experimental evidence for such a transition by conductivity measurements on granular Al-Ge specimens[6–8] in the vicinity of the metal-insulator transition. We report for the first time the existence of a range of metal concentrations for which the samples are strongly localized (exponential localization) in the normal phase and yet undergo a superconducting transition. This result is interpreted in comparison with other granular systems like Al-Al_2O_3 which do not display superconductivity when they are strongly localized. This difference in behavior is related to the difference in grain sizes[8–9] (~ 120 Å in Al-Ge and ~ 30 Å in Al-Al_2O_3). We discuss the semiconductor-superconductor transition in terms of the intergrain coupling energy V_L, the Josephson coupling energy E_J, the Coulomb charging energy E_C, and the splitting between the electronic levels δ at the Fermi level in the single grain. A necessary condition for the occurrence of the transition is that $E_J > E_C > V_L$. Experimentally, this can be achieved for large enough grains in a narrow range of metal concentration near the metal-insulator transition.

Samples were prepared by coevaporation of Al and Ge on glass substrates at room temperature from two electron beam guns.[8] The rate of each gun was individually monitored and regulated in order to obtain predetermined ratios. Using suitable masks we obtained in each evaporation nine samples with a concentration variation of 1–2%, from sample to sample. Thus the relative concentrations in each evaporation were known quite accurately, but there is a larger error in the absolute values. The combined evaporation rate was 30–50 Å/sec and the samples were about 2000 Å thick. The pressure before evaporation was 10^{-6} Torr. The characteristics of all samples are listed in Table I.

At each evaporation TEM samples were simultaneously evaporated onto SiO films held at room temperature. Figure 1 shows a typical TEM micrograph. It can be seen that the Al grains are embedded in the Ge matrix. Figure 2 gives a histogram of grain sizes and includes a best fit to a normal distribution of the histogram. Notice that the distribution of grain size is quite narrow in contrast to other granular systems.

The electrical resistivity as a function of temperature was measured by a four-contact method, with a measuring current of 10 μA. For high-resistance films we used only two-point contact with a Keithley 616 electrometer.

Figure 3 depicts $\ln\rho$ (ρ is the normal-state resistivity of the samples) as a function of temperature for the samples presented in Table I. Note that at low temperatures there is a transition from superconducting films to semiconducting ones. For high metal concentrations the superconducting transition temperature is nearly constant (independent of metal concentration) and about 1.8 K. For still larger metal concentration the transition temperature falls down to that of bulk Al (1.2 K).

TABLE I. t—sample thickness; C—metal volume concentration; ρ_{RT}—the normal-state resistivity at room temperature; ρ_{LH}—the normal-state resistivity at 4.2 K. All samples are evaporated on glass substrates except for sample K, which is evaporated on Mylar substrate.

Sample	t (kÅ)	C (%)	ρ_{RT} (Ω cm)	ρ_{LH} (Ω cm)
A	2.17	67.5	0.0074	0.016
B	2.13	65.5	0.0141	0.051
C	2.09	63.4	0.0251	0.200
D	2.60	66.8	0.0095	0.023
E	2.59	64.7	0.0173	0.084
F	2.57	62.6	0.0285	0.278
K	2.35	66.3	0.0094	0.0169

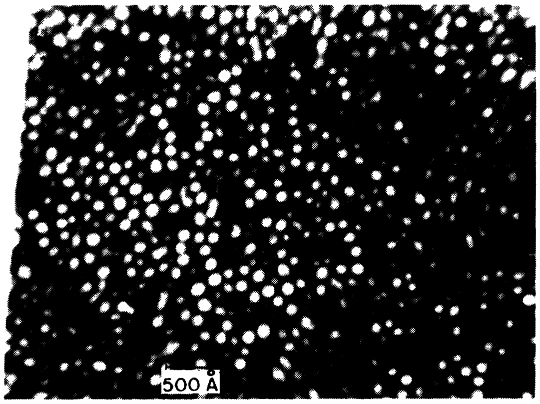

FIG. 1. Typical TEM micrograph. The grains are Al and the background is Ge (amorphous).

We can follow the metal-insulator transition as a function of metal volume concentration. While samples *C* and *F* are semiconducting, down to our lowest temperature, the other samples exhibit a superconducting transition with a decreasing transition temperature as the metal concentration is reduced. We attribute the decrease in T_c to the buildup of Coulomb charging energy as the metal concentration is lowered and the insulating barriers between neighboring grains become thicker.[10]

We now turn our attention to the possibility of a semiconductor-superconductor transition as a function of temperature. Inspecting Fig. 3, we see that sample *E* is on the edge of superconductivity. By a small change of 1.3% in the metal concentration, we get a semiconducting sample (see Table I and Fig. 3). Figure 4 shows a plot of *R* vs *T* for sample *E*. The transition from a semiconducting behavior to a superconducting state is very prominent. The semiconducting behavior is well demonstrated by the high negative temperature coefficient of resistance which must be the result of a thermally activated process.

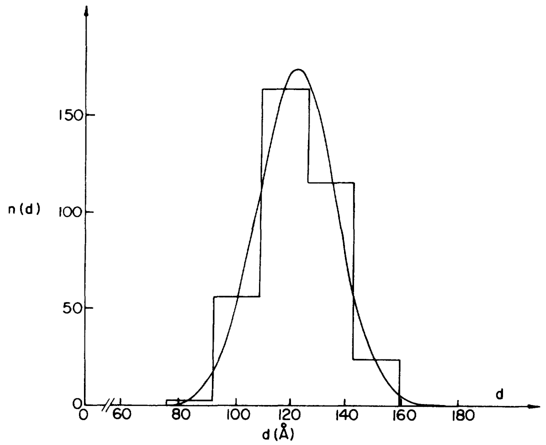

FIG. 2. Histogram of a distribution of grain size including a best fit to a normal distribution of the histogram. The data were taken from a micrograph of sample *B* (see Table I).

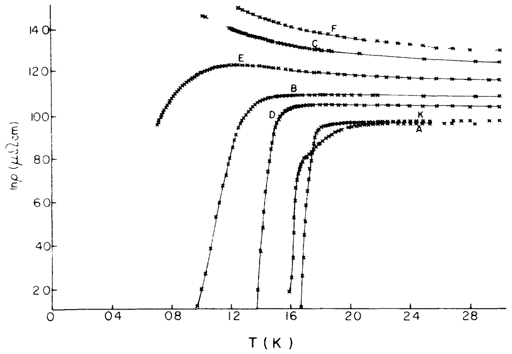

FIG. 3. lnρ as a function of temperature for all the samples of Table I.

A thermally activated conductivity accompanied by a superconducting transition was already observed for Al-Al_2O_3 samples.[4,5] One of the main results was that a superconducting transition is observed in the metallic and weak localization regimes, but not in the case of strong localization. Here the strong localization regime is characterized by an exponential dependence $R(T) \propto \exp[-(T_0/T)^{1/2}]$, while the weak localization regime is characterized by a weaker dependence, usually logarithmic, but in any case less than exponential. In Fig. 5 we present a plot of ln*R* vs $1/T^{1/2}$ for sample *E*. We can see that for this sample the dependence of *R* is an exponential with at least $1/T^{1/2}$ behavior. The data are also compatible with $R \propto \exp -(T_1/T)$. Thus we can conclude that sample *E* is in the strong localization regime and truly insulating in the normal phase.

We have considered the possibility that superconductivity occurs only in some metallic threads in the sample rather than being a bulk semiconductor-superconductor transition. We have rejected this possibility for several reasons. Such metallic threads would at some low temperature start to short out the whole sample. No such behavior was observed.

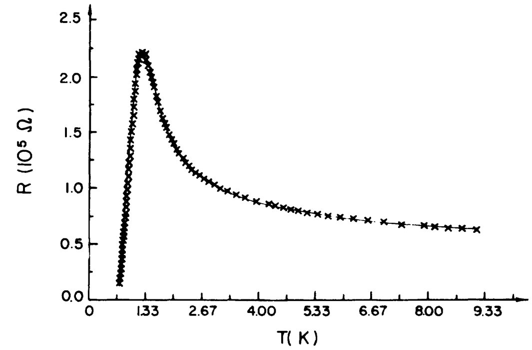

FIG. 4. Resistance *R* as a function of temperature for sample *E*.

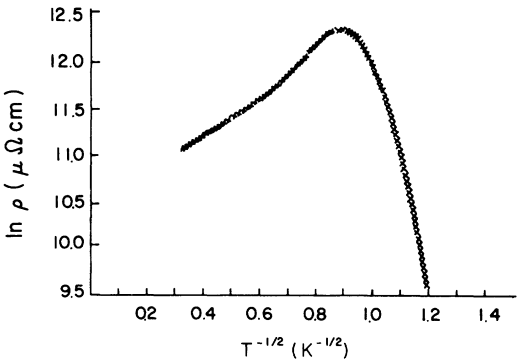

FIG. 5. The logarithm of the resistance R as a function of $(1/T)^{1/2}$ for sample E. The data are also compatible with $\ln R \propto (1/T)$, but not with a temperature dependence weaker than exponential.

Moreover, the resistivity of the sample shown in Fig. 4 is more than 0.2 Ω cm, while typical values for Al films range from 2.10^{-6} Ω cm for clean films up to 10^{-3} Ω cm for very dirty metallic ones. We doubt that there could be such gross inhomogeneities in one sample. From Figs. 1 and 2 we can see that they are very homogeneous as compared to other samples,[7,9] and that the distribution of grain size is quite narrow. Moreover, the narrow range of metal concentrations (4%, see Fig. 3 and Table I) over which the system changes its behavior from superconductivity to semiconductivity can only result from a quite homogeneous structure.

From the above discussion we can conclude that sample E does indeed undergo a semiconductor-superconductor transition. This means that when Al grains become superconducting the Josephson coupling energy E_J between them is larger than the regular tunneling coupling energy V_L, since the latter is not large enough to obtain a metallic behavior. We can write both energies in terms of t, the tunneling matrix element between grains[1]:

$$V_L = 2\pi |t|^2/\delta \; , \tag{1}$$

$$E_J = \pi^2 |t|^2 \Delta(T=0)/2\delta^2 \; , \tag{2}$$

where $\Delta(T=0)$ is the superconducting energy gap at $T=0$ and δ the splitting between the electronic levels due to the finite grain size. Equating V_L and E_J we get

$$\frac{\pi}{4}\Delta(T=0) = \delta \; . \tag{3}$$

Using Eq. (3) and introducing d^3, where d is the grain diameter, to compute δ, one gets for d a critical value d_c, as already noticed in Refs. 2 and 4:

$$d_c = \left[\frac{3}{\pi^2 N(0)\Delta(T=0)} \right]^{1/3} \; .$$

Here $N(0)$ is the electronic density of states at the Fermi level in the grains. For Al grains the condition $E_J > V_L$ is met when $D > d_c \sim 75$ Å. This can explain the clear evidence for a semiconductor-superconductor transition in Al-Ge films with grain size of about 120 Å (Fig. 1) and the more ambiguous behavior for Al grains of about 30 Å.[3,5,9] It is interesting to note that Eq. (3) up to a numerical factor of order unity is also the criterion for the existence of one Cooper pair per grain. The physical interpretation of Eq. (3) then is that, as soon as superconductivity is well established in each grain, the Josephson coupling energy is always larger than the tunneling coupling energy.

What remains to be explained is the narrow range of metal concentrations over which the semiconductor-superconductor occurs. There are two energies that drive the metal-insulator transition: The splitting between the electronic levels δ ($\delta \simeq 0.5$ K in our samples), and the electrostatic charging energy of the grains. For isolated 120-Å grains in an Al_2O_3 matrix, $E_c \simeq 100$ K. However, due to the divergence of the dielectric constant, E_c goes to zero at the metal-insulator transition.[11] In a small concentration range, E_c varies from 0 to a few K, at which point it becomes larger than E_J and V_L, and the sample is insulating.

In conclusion, we wish to emphasize that a large grain size plays two distinct roles for the existence of a semiconductor-superconductor transition in granular materials: (1) It allows the Josephson coupling energy to be larger than the regular tunneling coupling energy, a situation which is acheived as soon as there is, on the average, more than one Cooper pair per grain, and (2) it opens up the range of metal concentrations near the metal-insulator transition where the Coulomb interactions are not large enough to suppress superconductivity. We note, finally, that E_J is temperature dependent. While $E_J(T=0)$ is the relevant quantity for determining the occurrence of the semiconductor-superconductor transition, $E_J(T)$ will determine the effective transition temperature.

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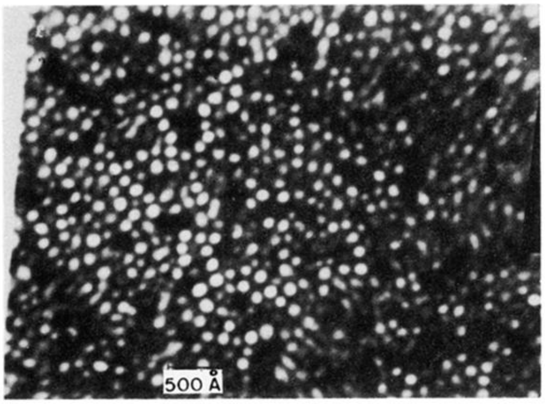

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