Superconducting properties, conductivity, and structure of granular metal-insulator films

I. M. Dmitrenko, A. M. Glukhov, T. A. Kovalenko, A. E. Kolin'ko, and N. Ya. Fogel'

Physicotechnical Institute of Low Temperatures, Academy of Sciences of the Ukrainian SSR, Kharkov
(Submitted 15 August 1985; resubmitted 9 January 1986)
Zh. Eksp. Teor. Fiz. **90**, 2065–2076 (June 1986)

An investigation was made of the critical temperatures T_c, temperature dependences of the resistance in the normal state, and structure of granular metal (In,Sn)-insulator(GeO,SiO) films. The Sn–GeO system was investigated in greatest detail in the range of insulator concentrations from 0 to 55 vol.%. The composition dependence of T_c was a curve with a maximum. It was found that the experimental data on the lowering of T_c were in good agreement with a model that allows for fluctuations of the modulus of the order parameter of granular systems with Josephson coupling between the grains; when the coupling was strong, the influence of fluctuations of the electromagnetic field was also important. An increase in T_c was observed only at insulator concentrations sufficiently low to ensure a direct metallic coupling between grains.

1. INTRODUCTION

The superconductivity of granular metal films is attracting interest because such films provide an opportunity for verifying new physical ideas (localization of electrons in two-dimensional systems and its influence on superconducting properties of films,[1,2] and topological phase transitions in two-dimensional superconductors[3–6]). Major progress has been made in the theory of granular media that allows for the influence of the electrostatic effects[7–10] that destroy the Josephson coupling between grains, i.e., the coherent state in the granular system. A theoretical study has begun of granular media near the percolation threshold corresponding to a transition to a bulk (nongranular) state.[11,12]

In experimental studies of the physics of granular superconductors it is convenient to employ systems with properties (grain size, transparency of the intergrain gaps) that can be varied in a controlled manner and in a wide range. They include granular metal and insulator films in which the parameters of the medium can be controlled by varying the insulator concentration. Systems of this kind have been investigated in detail from the structural point of view and from the point of view of the conduction mechanisms.[13] Experimental studies of superconducting properties of such systems are now attracting attention.[14–16]

We shall report a detailed study of the temperature of the superconducting transition and of the temperature dependences of the normal-state resistance of granular Sn-GeO, In-GeO, and In-SiO films. We shall also report a determination of the structure characteristics of these films. We shall discuss the experimental results in the light of recent topical aspects of the physics of granular superconductors.

2. PREPARATION OF SAMPLES AND EXPERIMENTAL METHOD

We investigated two-component granular films prepared by simultaneous evaporation of a metal and an insulator on pyroceram substrates kept at room temperature in 10^{-6} Torr vacuum. The components were evaporated from two different sources. Use was made of a method of variable-composition films which made it possible to evaporate up to 30 samples with different insulator concentrations in a single run. The distribution of the composition in a batch of samples prepared by simultaneous condensation of two components was deduced from the distribution of thickness of each of them. The distribution of thicknesses of reference samples of metal and insulator films was determined by two methods: the Tolansky interferometric method and the method involving determination of the transparency of films with an MF-4 microphotometer. The absolute values of the film thicknesses and compositions were deduced from the results of measurements made with two quartz thickness meters, on one of which only a metal was deposited and on the other only an insulator. The thicknesses and compositions of two-component samples prepared in the same batch were found from measurements of the "thickness" of each of the components for samples which were located symmetrically (together with the quartz meters) relative to the evaporators and from calibrated distributions of the thicknesses of the individual components. The thicknesses in each batch of samples were varied within the range 400–800 Å. The use of films of variable composition minimized the relative error in the determination of compositions of all samples in a given batch and the preparation of a batch of samples under perfectly identical conditions avoided the accidental scatter of the film properties.

All the electrical measurements were carried out by the four-probe method. The superconducting transitions were detected with the temperatures kept and measured to within 3×10^{-3} K. In the determination of the temperature dependences of the resistance R in the range 4.2–200 K the temperature stabilization and measurements were accurate to within ~ 0.1 K. The electrical circuitry used in this study made it possible to carry out simultaneous measurements on 26 samples belonging to the same batch. This reduced signif-

 0038-5646/86/061210-07$04.00

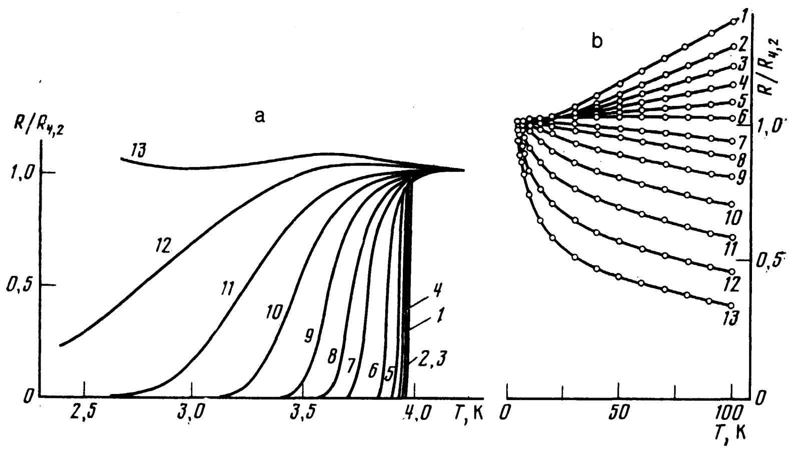

FIG. 1. Temperature dependences of the resistance of batch No. 1 Sn-GeO samples of different compositions in two temperature ranges: a) 2.4–4.2 K; b) 4.2–100 K. Insulator concentration in volume percent: 1) 13.6; 2) 15.9; 3) 17.4; 4) 19.2; 5) 21; 6) 23.1; 7) 25.2; 8) 26.3; 9) 27.4; 10) 28.4; 11) 29.5; 12) 30.5; 13) 31.6. The curves in Fig. 1a were recorded using automated apparatus.

icantly the relative error of the measurements carried out on samples with different compositions.

It was established that superconducting transitions in granular Sn–GeO films were sensitive to the value of the measuring current. An increase in the current shifted the whole transition down on the temperature scale. Control measurements on the same samples carried out not in liquid but in gaseous helium indicated that this shift was not due to thermal effects. Right down to the currents of $\sim 10^{-3}$ A there was no heating of these samples as a result of the Joule effect. The transition shift was due to the fact that the passage of an electric current through a granular system weakened the Josephson coupling between the grains. Since we were interested in the case of weak coupling between the grains, the main measurements were carried out employing a current of 100 μA when the reduction in the critical temperature T_c was a readily observable effect.

Investigations of the structure were carried out using a UEM-7A microscope on the same samples for which the electrical properties were determined.

3. EXPERIMENTAL RESULTS

Figure 1 shows typical temperature dependences of the normalized film resistance $R/R_{4.2}$ in the region of the superconducting transition and in the range 4.2–100 K; these results were obtained for one batch of Sn-GeO samples of variable composition. The curves are labeled in the increasing order of the insulator content. The dependence of the electrical resistivity on the insulator content is shown for the same batch in Fig. 2. It is clear from Fig. 1b that an increase in the GeO content in the films resulted in a transition from the metallic to the insulating behavior in the resistance. In the intermediate region (20–25 vol.% GeO) the temperature dependence of the resistance was complex. The ratio of the resistance at $T = 293$ K to that at 4.2 K, $r = R_{293}/R_{4.2}$, representing the magnitude and sign of the temperature coefficient of the resistance, fell monotonically on increase in the GeO content.

Figure 1a shows that in the presence of relatively small amounts of GeO the temperature T_c of the composite films increased, but a further increase in the insulator concentration C shifted the superconducting transition curves toward lower temperatures. At high values of C the superconducting transition was incomplete or did not occur at all [there was only a small singularity in the dependence $R(T)$]. An increase in the insulator concentration not only shifted T_c but altered the width of the superconducting transition. The dependences[1)] of the transition temperatures T_c of freshly prepared Sn-GeO films on the ratio r and on the insulator concentration are plotted in Figs. 3 and 4 (curve 1) for several batches of granular Sn-GeO films. It was found that a reduction of r or an increase in C first increased the transition temperature and then caused a monotonic fall; after reversal of the temperature coefficient of the resistance the values of T_c became lower than T_c for pure single-component Sn films. The maximum value of T_c was observed at about 15 vol.% GeO and it was 4.01 K.

An aging effect was exhibited by granular films when they were stored at room temperature. After aging the transition temperature T_c of films with low GeO concentrations ($C < 17\%$) fell, whereas T_c of films with high insulator concentrations increased. Annealing of the samples for 2 h at $T = 140$ °C reduced considerably the resistance and increased T_c. This effect is demonstrated in Fig. 4 (curve 2), which gives the dependences of T_c on the GeO concentra-

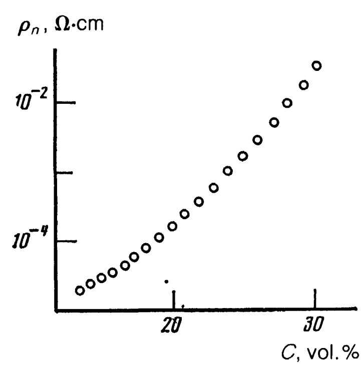

FIG. 2. Dependence of the electrical resistivity (Ω·cm) on the insulator concentration in batch No. 1 samples of Sn-GeO.

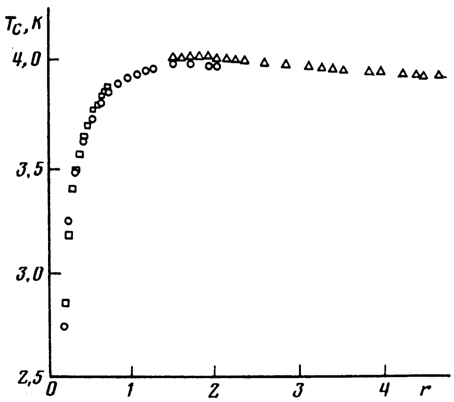

FIG. 3. Dependence of the superconducting transition temperature on the ratio $r = R_{293}/R_{4.2}$ for several batches of Sn-GeO films: ○) batch No. 1; △) No. 2; □) No. 3.

tion for the same batches of samples in the freshly condensed and annealed states.

A study of the superconducting transitions in In-GeO (insulator concentration 25–35%) and In-SiO (10–19%) composite films revealed that in the case of the former films in this range of concentrations the superconducting transition temperature was considerably higher than for bulk indium, whereas in the case of the films containing SiO there was a basically opposite tendency (Fig. 5). In the films containing indium as the metal component there was no correlation between the sign of the shift of T_c and the temperature coefficient of the resistance. The temperature coefficient of the resistance remained positive at these very high values of ρ_n, as was also true of Sn-GeO samples. In the case of In-GeO

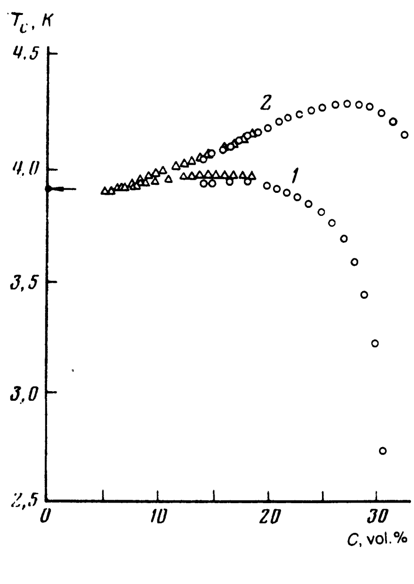

FIG. 4. Dependences of the superconducting transition temperature on the insulator concentration for Sn-GeO films. The designation of the batches is the same as in Fig. 3: 1) freshly prepared films; 2) the same films after annealing in vacuum for 2 h at 140 °C. The arrow on the abscissa is the critical temperature of a pure tin film of 550 Å thickness.

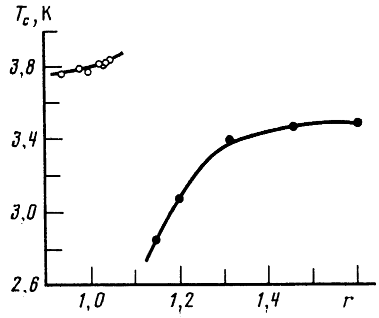

FIG. 5. Dependence of the superconducting transition temperature on $r = R_{293}/R_n$ for In-GeO (○) and In-SiO (●) films.

films the maximum positive shift of the transition temperature T_c was 0.44 K.

In addition to these electrical measurements, we also carried out a study of the structure of the samples. The electron diffraction data indicated that the insulator component of the films was amorphous. A gradual increase in the insulator concentration resulted in strong broadening of the electron diffraction rings representing the metal component of the films and weakened the intensities of the rings corresponding to higher orders. These results indicated a considerable reduction in the size of the coherent scattering regions on increase in the insulator concentration. According to the results of electron microscopy obtained for the range $C = 9$–26%, the metal component in the film formed a complex branched network with embedded insulators. At higher insulator concentrations the Sn-GeO film system exhibited a typical granular structure and at $C \gtrsim 37\%$ the average grain size was practically independent of C and amounted to ~ 50 Å.

In the case of In-SiO films the structure depended strongly on that observed for Sn-GeO. Throughout the investigated concentration range the In-SiO films consisted of grains with a wide range of sizes from 100 to 2000 Å. Large grains were surrounded by insulator layers 500–2000 Å thick, with many smaller embedded grains. The structure of In-GeO films had not yet been investigated.

4. DISCUSSION OF RESULTS

Depression of T_c The characteristic features of the structure of granular media are such that we can expect a great variety of mechanisms that can enhance or suppress the superconductivity; these mechanisms are associated with the smallness of the metal particles and the nature of their coupling.

We shall first consider the depression of T_c exhibited by Sn-GeO films with $r < 1$. We shall begin by considering the possible role of the Coulomb effects. The discrete nature of the charges on the grains should give rise to an activated temperature dependence of the conductivity σ of a granular medium and this dependence of σ should be[17]

$$\sigma \propto \exp(-E_q/kT) \quad \text{for} \quad E_q < kTD/a. \tag{1}$$

Here, D is the distance between grains, a is the interatomic distance, E_q is the Coulomb energy amounting to

$$E_q = e^2/2C_g, \tag{2}$$

and C_g is the capacitance of a grain.

The depression of T_c because of the Coulomb mechanism in the $E_q/E_q^c \ll 1$ case is given by the expression[7]

$$(T_{c0}-T_c)/T_{c0} = [21\zeta(3)/8\pi\gamma_0]E_q/E_q^c. \tag{3}$$

Here, T_{c0} is the transition temperature in the bulk metal; $\ln\gamma_0$ is the Euler constant; $\zeta(3) = 1.202$; $E_q^c = \Delta_0/4$; Δ_0 is the superconducting gap at $T = 0$.

Since both the shift of T_c and the temperature dependence of σ are described by expressions with the same parameter E_q, we can try to account for the role played by the charge in the depression of T_c on the basis of the experimental results. We obtained relevant estimates for one of the batches of Sn-GeO films. In the range $C \lesssim 40$ vol.% GeO the experimental temperature dependences $\sigma(T)$ did not agree with Eq. (1). In the case of the films with $C \geqslant 45\%$ the experimental results were described approximately by Eq. (1) above T_c, but only in a very limited temperature range (up to ~ 7 K). Estimates of the Coulomb energy E_q obtained from Eq. (1) and the experimental results for this temperature range gave $(0.17–1.05)\times 10^{-16}$ erg, where E_q increased on increase in C. These estimates indicated that at $T \geqslant 10$ K the Coulomb energy became less than the absolute temperature. Therefore, it was difficult to expect Eq. (1) to be satisfied in the range $T \gtrsim 10$ K.

The energies E_q estimated from the experimental results were much smaller than the critical Coulomb energy $E_q^c = \Delta_0/4 \approx 2.3\times 10^{-16}$ erg, i.e., the condition of validity of Eq. (3) in the form $E_q \ll E_q^c$ was basically well satisfied. However, the shift of T_c calculated with the aid of Eq. (3) was much smaller than that found experimentally. Therefore, the charge effect cannot account for the depression of T_c. In the normal state the charge effect is manifested only in a very narrow temperature range.

It should be noted that the estimates of the Coulomb energy obtained from the experimental results were considerably smaller than the Coulomb energy obtained from the experimental results were considerably smaller than the Coulomb energy of an isolated grain given by Eq. (2), for which the capacitance C_g of small particles was of the order of their diameter L($E_{qg} \sim 10^{-12}$ erg for grains of ~ 50 Å size). An estimate of E_q allowing for the capacitance of the intergrain gaps[8] failed to alter significantly the estimate obtained above for isolated grains. Thr reasons for the discrepancy between the theoretical estimate of E_q and the values deduced from the experiments will be discussed later.

The Josephson coupling energy can be estimated from[8]

$$E_j = \hbar\Delta_0/8e^2R_j, \tag{4}$$

where $R_j = \rho_n/(L+s)$ (ρ_n is the electrical resistivity in the normal state and s is the distance between grains). In estimates the value of s can be ignored compared with L. In the case of samples with high GeO concentrations with $\rho_n = 10^{-2}\,\Omega\cdot$cm and $L \approx 5\times 10^{-7}$ cm, we find that Eq. (4) yields $E_j \approx 2.3\times 10^{-17}$ erg. Therefore, $E_j < E_q$ and, in accordance with the Abeles criterion,[8] the granular system should not exhibit superconductivity. However, the authors of several later theoretical treatments[9,10,18] have shown that the Abeles criterion can be greatly relaxed. For example, Akopov and Lozovik[18] used the self-consistent harmonic approximation for an ordered lattice of grains and showed that the condition of existence of the coherence in a granular system at $T = 0$ is the inequality $E_j/E_q \gtrsim 0.07$. At temperatures other than absolute zero the screening effect makes this criterion even less stringent.[9,10]

It is clear from the above estimates of E_j and E_q that even if $E_q > E_j$ the ratio of these two quantities satisfies the condition of stability of a granular superconductor $E_j/E_q \gtrsim 0.07$ obtained in Ref. 18. This condition is not satisfied by samples with high values of C for which the transition to the superconducting state is either incomplete or does not occur (curves 12 and 13 in Fig. 1a).

We shall show later that a fully satisfactory description of our experimental results is provided by models which completely ignore the Coulomb effects. The depression of T_c due to fluctuations of the modulus of the order parameter[19] of granular systems in which grains are coupled by the Josephson interaction should depend on the strength of the coupling between metal particles. Granular superconductors are called strongly or weakly coupled when they satisfy the conditions $\xi(0) \gg L$ and $\xi(0) \ll L$, respectively[19] [$\xi(0)$ is the coherence length at $T = 0$]. In the case of a strong Josephson coupling the shift $\mathscr{E}_s^s$ of the transition temperature [$\mathscr{E}_s^s = (T_{c0} - T_c)/T_{c0}$] due to fluctuations of the modulus of the order parameter is given by the expression[19]

$$\mathscr{E}_s^s = (\mathscr{E}_{c3})^{1/2}, \tag{5}$$

where $\mathscr{E}_{c3}$ is the width of the critical region for the three-dimensional case, which—according to the Ginzburg criterion[20–21]—is:

$$\mathscr{E}_{c3} = (1/32\pi^2)[k/\Delta c\xi^3(0)]^2. \tag{6}$$

Here, ΔC is the jump in the specific heat at the phase transition point. Combining Eqs. (5) and (6) and using formulas from the theory of free electrons, we obtain the following expression for $\mathscr{E}_s^s$ in the dirty limit:

$$\mathscr{E}_s^s = \left[\frac{2{,}4\pi^2\hbar^3 kT_{c0}\rho_n^3}{m_{eff}^4 v_F^5 A_0^3}\right]^{1/2}, \tag{7}$$

from which it follows that the shift of T_c should be proportional to $\rho_n^{3/2}$ ($A_0 = \rho_n l$ is constant for a metal and l is the mean free path of electrons).

Figure 6 shows the experimental dependence of T_c on $\rho_n^{3/2}$. Some of the data in the range of relatively low values of ρ_n can be described quite satisfactorily, in the qualitative sense, by the approximation dependence (7). In a numerical comparison of the experimental results with the theory we shall assume that $\rho_n l = 1.5\times 10^{-11}\,\Omega\cdot\mathrm{cm}^2$ (Ref. 22),

$v_F = 10^8$ cm/sec, and $m_{\rm eff} = m_0$. Then, Eq. (7) reduces to (with ρ_n in units of $\Omega\cdot$cm)

$$\mathscr{E}_s^s = 7.8\cdot 10^2 \rho_n^{3/2}.$$

It follows from the experimental straight line 1 in Fig. 6 that

$$\mathscr{E}_{s\ \rm exp}^s = 3{,}4\cdot 10^2\ \rho_n^{3/2}.$$

This numerical discrepancy between the theoretical estimate and the experimental results is not very significant.

The values of T_c for films with $\rho_n \geqslant 3\times 10^{-3} \Omega\cdot$cm deviate from the straight line 1 in Fig. 6. We shall assume that this deviation is due to a change to the weak coupling regime and compare the results obtained with the theory of the weak coupling limit. In this limit the shift of T_c is given by[19]

$$\mathscr{E}_s^w = 0{,}106/kT_{c0}\xi^2(0)L. \tag{8}$$

It follows from Eqs. (5) and (8) that the relationship between $\mathscr{E}_s^s$ and $\mathscr{E}_s^w$ is

$$\mathscr{E}_s^w = \mathscr{E}_s^s \xi(0)/L. \tag{9}$$

Bearing in mind that $\xi(0) = 0.85(\xi_0 l_{\rm eff})^{1/2}$, where $\xi_0 = 2.56\times 10^{-5}$ cm for Sn (Ref. 23), and using the same parameters as before, we obtain the following numerical estimate of $\mathscr{E}_s^w$:

$$\mathscr{E}_s^w = 1.51\cdot 10^{-8} \mathscr{E}_s^s / L\rho_n^{1/2} \tag{10}$$

The experimental data for samples with high GeO concentrations may be compared with this formula if we use the average grain size L as the fitting parameter. The best agreement between the experiments and Eq. (10) is obtained for $L = 30$ Å. Figure 6 shows the calculated curve 2 corresponding to Eq. (10) with $L = 30$ Å and to the values of $\mathscr{E}_s^s$ obtained by extrapolation of the experimental data for films with relatively low values of ρ_n. We can see that all the experimental results on the depression of T_c for Sn-GeO films can be explained satisfactorily by assuming that the shift of T_c exhibited by a granular superconductor with the Josephson coupling between grains is of fluctuation origin if the approximation of a strong coupling is assumed for some of the films and that of a weak coupling for other films.[2] It should be stressed that in both limits we are using the same properties and the same fitting parameter which is needed in comparing the results with the theory of Ref. 19 in the limit of weak coupling (this parameter is the average size of the grains). The value of L ensuring the best agreement between the calculated curve 2 and the experimental points agrees quite well with the electron microscopy data.

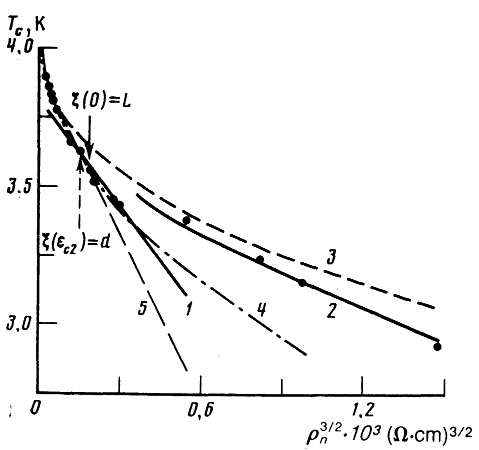

FIG. 6. Dependence of the superconducting transition temperature on $\rho_n^{3/2}$ for Sn-GeO samples. Curve 1 is drawn through experimental points; curve 2 is calculated from Eq. (10) assuming that $L = 30$ Å; curve 3 corresponds to Eq. (11) with $T_{c0} = 3.98$ K; curve 4 is plotted in accordance with Eq. (12) with $T_{c0} = 4.05$ K; curve 5 represents Eq. (13) with $T_{c0} = 3.98$ *K*.

Using $L \approx 30$ Å we can estimate the value of ρ_n at which there should be a change from the strong to the weak coupling regime. The value of $\rho_n = 3\times 10^{-3} \Omega\cdot$cm corresponding to $\xi(0) = L$ is identified by an arrow in Fig. 6. It is clear that some fo the investigated films correspond to $\xi(0) > L$, whereas others correspond to $\xi(0) < L$. The strong inequality $\xi(0) \ll L$ is satisfied only when the insulator concentration is $\gtrsim 50\%$ and the samples are nonsuperconducting. An estimate of the critical temperature for these samples obtained on the basis of the theory of Ref. 19 in the weak coupling approximation gives $T_c \lesssim 1$ K. However, in this case we can no longer ignore the Coulomb effect, as pointed out above.

In the case of In-SiO films the behavior of T_c is in qualitative agreement with Eq. (7) in the same range of the resistivities of ρ_n as for Sn-GeO samples, whereas at high values of ρ_n a deviation from this approximation is observed. Granular Al films investigated earlier[15] also exhibit a change from the strong to the weak coupling between grains in the range of ρ_n from 10^{-3} to 10^{-2} $\Omega\cdot$cm and the value of T_c decreases on increase in ρ_n.

We can thus see that in spite of the irregular structure of the investigated coupled films, the depression of T_c can be described quite satisfactorily by the model of a fluctuation shift of T_c developed for a regular three-dimensional granular superconductor where the grains are coupled by the Josephson interaction.[19]

However, we must bear in mind that in addition to fluctuations of the order parameter, the transition temperature may be also depressed by fluctuations of an electromagnetic field. This effect has been investigated theoretically for continuous high-resistivity films.[24,25] According to a calculation reported by Kulik,[26] fluctuations of an electromagnetic field reduce T_c for a single Josephson contact between two identical superconductors. There is no doubt that this effect should apply also to a granular medium. The dashed curve 3 in Fig. 6 is calculated using the Kulik formula[24] allowing for fluctuations of an electromagnetic field:

$$-\frac{\Delta T}{T_{c0}} = \frac{R_n^\square}{8R_c^\square} \ln\left(\frac{8R_c^\square}{R_n^\square}\right). \tag{11}$$

Here, $R_n^\square$ is the film resistance per square, where $R_c^\square = 4.12$ kΩ. In comparing this theory with the experimental results we shall use T_{c0} as the fitting parameter. It follows from Fig.

6 that in the case of relatively highly conducting Sn-GeO films, which are closest in their properties to continuous films, the experimental results agree well with Kulik's theory. In the case of films with a more pronounced granular structure the theory and experiment agree qualitatively. Simultaneous allowance of fluctuations both of an electromagnetic field and of the order parameter within the framework of the theory of continuous films[26] shows that the contributions of the two mechanisms of the depression of T_c should be additive. Then, instead of Eq. (11), we can write down in accordance with Eq. (24):

$$-\frac{\Delta T}{T_{c0}}=\frac{R_n^\square}{8R_c^\square}\ln\left(\frac{8R_c^\square}{R_n^\square}\right)+\mathscr{E}_{c2}\ln\left(\frac{1}{\mathscr{E}_{c2}}\right), \tag{12}$$

where $\mathscr{E}_{c2}\approx 0.04\, R_n^\square/R_c^\square$ is the width of the critical region for a two-dimensional superconductor. The fluctuations in superconducting films are two-dimensional if $d\ll\xi(T)$ (d is the film thickness). At low temperatures all the investigated samples are undoubtedly three-dimensional because $\xi(0)\ll$d. The coherence length $\xi(T)$ rises strongly on approach to T_c. For some of the samples (experimental points in Fig. 6 located to the left of the dashed arrow) the condition $d<\xi(T)$ is met at the limit of the critical temperature interval $\mathscr{E}_{c2}$ and we can use Eq. (12). The calculated curve 4, which corresponds to Eq. (12), is shown as a chain in Fig. 6. In this case the fitting parameter was again T_{c0}. The values of T_{c0} which were used to calculate the theoretical curves 3 and 4 were close to the maximum transition temperature 4.02 K for simultaneously evaporated Sn-GeO films. It is clear from Fig. 6 that in the case of a sufficiently strong Josephson coupling between grains Eq. (12) again describes very well the experimental results. In the case of the model of Deutscher, Imry, and Gunther[19] an allowance is made for three-dimensional critical fluctuations of the order parameter of a strongly coupled granular medium, whercease in the work of Kulik these fluctuations are assumed to be two-dimensional. In the case of extremely dirty semiconductors with $l\lesssim a$ the values of $\mathscr{E}_{c3}$ and $\mathscr{E}_{c2}$ are of the same order of magnitude. Since the theoretical estimates of $\mathscr{E}_c$ for two- and three-dimensional superconductors are vlaid only within a certain range of the numerical coefficients and the available experimental results cannot be used to give a decisive preference to one of the theories (Ref. 19 or Ref. 24), the problem of dimensions of fluctuations in the investigated films in the case of a strong Josephson coupling between grains remains unresolved.

A much poorer agreement is obtained when the experimental results are compared with the theory of Ref. 25, which also considers the fluctuation-induced shift of T_c, but makes allowance not only for the effects discussed in Ref. 24, but also for longitudinal vibrations associated with a scalar potential. According to Ref. 25, the negative shift of T_c is given by the expression

$$-\frac{\Delta T}{T_{c0}}=\frac{R_n^\square}{4\pi^2R_c^\square}\left\{\frac{14\zeta(3)}{\pi^2}\ln\left(\frac{16R_c^\square}{R_n^\square}-\frac{1}{3}\left[\ln\left(\frac{\hbar v_F l}{d^2kT}\right)\right]^3\right\}. \tag{13}$$

A calculation carried out using the above formula with the replacement of T by T_c in the second term and on the assumption that $T_{c0}=3.915$ K gives curve 5 in Fig. 6. We can see from Fig. 6 that in the case of low values of $R_n^\square$ the theoretical results of Refs. 24 and 25 are practically identical. At higher values of the film resistance the experimental results are described better by Kulik's theory.

We can thus conclude that the experimental results are in reasonable agreement with, on the one hand, the Josephson model[19] and, on the other, with the fluctuation theory of Kulik for continuous films. The two theories give similar results and this is due to the fact that the case of a strong coupling between grains differs little from the case of a continuous dirty film. It seems to us that the depression of T_c in those granular superconductors in which the Coulomb effects are unimportant can be described fully if the model of Deutscher, Imry, and Gunther is supplemented by an allowance for fluctuations of an electromagnetic field.

We shall consider particularly the problem that the majority of the theoretical descriptions of granular media is based on regular systems with identical metal particles and identical intergrain gaps, whereas in reality we are dealing with a stochastic granular medium.

It is clear that the Coulomb effects discussed theoretically in Refs. 7–10 are extremely sensitive to departures from the regularity in a medium. If metallic short-circuiting paths exist between some of the grains, then electrical charges can flow along these paths to the neighboring grains. The appearance of such paths gives rise to percolation trajectories which do not penetrate the whole granular medium but give rise to clusters consisting of many grains within which the charge can flow freely. The fact that the Coulomb energy found experimentally from the $\sigma(T)$ dependence in the normal state is several orders of magnitude less than the value calculated for individual grains is evidence that grains combine into clusters which are large compared with a single grain. Estimates of the cluster dimensions obtained from the experimental values of E_q show that $L_{cl}=10^{-4}$–10^{-2} cm if the permittivity is in the range $\varepsilon=1$–10. The possibility of combination of grains to form larger clusters has been confirmed experimentally[1,27] for granular Pb and Al films. In the limit when $L_{cl}\to L$ the superconducting properties of a granular medium should be largely determined by the charge effect.

The fact that the experimental results for irregular granular films are described well by a regular-structure model suggests that the results of Ref. 19 should not be greatly affected by stochasticity. According to Ref. 11, if the scatter of the strength of the coupling between the grains is small, then such a scatter should be averaged out by thermal fluctuations.

Elevation of T_c. We shall now consider the experimental results on the elevation of T_c. According to the structure data, all the granular films with low values of ρ_n show clearly the presence of a metal network. This should be allowed for in the explanation of the elevation of T_c.

The elevation of T_c of all the investigated granular films obviously cannot be attributed to the quantization of the electron or phonon spectra of small metal particles. The separation between the quantized energy levels of electrons is given by $\Delta E \approx E_F/N_g$ (Ref. 28), where N_g is the number of electrons in the bulk of a grain. Combination of grains into clusters and the presence of a metallic grid or of percolation paths makes N_g low, so that the value of ΔE should be low and spatial quantization should not be very effective. In view of the possibility of phonon propagation both in a metal network and through an insulator, the quantization of the phonon spectrum should not be manifested either. A comparison of our results with the experimental data of Ref. 29 for grid-like In films without an insulating filler shows that the presence of an insulator in our films is a very important factor. The results of Ref. 29 demonstrate that for any parameters of the grid structure in In films the values of T_c are lower than those for bulk In. The electron micrographs given in Ref. 29 and our own micrographs suggest that the nature of the metal network is very similar in the two cases. In the absence of the insulator the shift of T_c is negative,[29] whereas in its presence the shift is positive. The rise of T_c for grid films on evaporation of SiO on top of these films[29] may be attributed to filling of the grid cells with an insulator and formation of a structure similar to that found in granular films. It follows from our comparison that the elevation of T_c is likely to be due to the influence of the indirect interaction between electrons via virtual excitons in the insulator.[30]

Nor can we exclude the influence of a change in the phonon spectrum compared with the spectrum of a bulk metal. However, the experimental results which might be used in a comparison with the theories of Refs. 31–33 and which allow for this effect are not available. Undoubtedly, our experimental results should also be considered in the light of the percolation models of granular media.[11,12] We shall do this in a separate communication.

The authors are grateful to N. V. Zavaritskiĭ, I. O. Kulik, Yu. E. Lozovik, and R. I. Shekhter for valuable discussions and comments.

[1)] The critical temperature of each sample was determined in the middle of the transition, i.e., at the point $R = 0.5R_n$. If $R \neq$const above T_c, the value of R_n was determined for samples with a negative temperature coefficient of the resistance from the maximum value of R, whereas for those with a positive coefficient right up to T_c it was deduced from the downward deviation from the quasilinear dependence at low temperatures. In all cases the relative error in the determination of R_n was small and should not affect significantly the precision of determination of T_c.

[2)] Measurements of resistive transitions carried out for varius values of the current I (from 1 to 100 μA) indicated that for any fixed value of I the experimental dependences $T_c(\rho_n)$ agreed with Eqs. (7) and (10) in the limits of strong and weak coupling between the grains. However, when the transport current was reduced, the whole dependence shifted toward higher values of T_c and stronger coupling.

[1]A. F. Hebard and J. M. Vandenberg, Phys. Rev. Lett. **44**, 50 (1980).
[2]G. Deutscher, B. Bandyopadhyay, T. Chui, P. Lindenfeld, W. L. McLean, and T. Worthington, Phys. Rev. Lett. **44**, 1150 (1980).
[3]M. R. Beasley, J. E. Mooij, and T. P. Orlando, Phys. Rev. Lett. **42**, 1165 (1979).
[4]S. Doniach and B. A. Huberman, Phys. Rev. Lett. **42**, 1169 (1979).
[5]B. I. Halperin and D. R. Nelson, J. Low Temp. Phys. **36**, 599 (1979).
[6]Yu. E. Lozovik and S. G. Akopov, Solid State Commun. **35**, 693 (1980).
[7]I. O. Kulik and R. I. Shekhter, Fiz. Nizk. Temp. **2**, 21 (1976) [Sov. J. Low Temp. Phys. **2**, 9 (1976)].
[8]B. Abeles, Phys. Rev. B **15**, 2828 (1977).
[9]E. Šimanek, Solid State Commun. **31**, 419 (1979).
[10]K. B. Efetov, Zh. Eksp. Teor. Fiz. **78**, 2017 (1980) [Sov. Phys. JETP **51**, 1015 (1980)].
[11]A. G. Aronov, M. E. Gershenzon, and Yu. E. Zhuravlev, Zh. Eksp. Teor. Fiz. **87**, 971 (1984) [Sov. Phys. JETP **60**, 554 (1984)].
[12]L. B. Ioffe, Zh. Eksp. Teor. Fiz. **80**, 1199 (1981) [Sov. Phys. JETP **53**, 614 (1981)].
[13]B. Abeles, M. D. Ping Sheng Coutts, and Y. Arie, Adv. Phys. **24**, 407 (1975).
[14]J. J. Hauser, Phys. Rev. B **3**, 1611 (1971).
[15]T. Worthington, P. Lindenfeld, and G. Deutscher, Phys. Rev. Lett. **41**, 316 (1978).
[16]V. P. Alekseevskiĭ, E. I. Balabanov, B. P. Bespalov, V. R. Gakel, A. S. Kostromin, V. A. Mikheev, L. I. Pechentkovskaya, V. V. Titov, and V. V. Yarosh, Fiz. Nizk. Temp. **4**, 1072 (1978) [Sov. J. Low Temp. Phys. **4**, 509 (1978)].
[17]R. I. Shekhter and I. O. Kulik, Fiz. Nizk. Temp. **1**, 435 (1975) [Sov. J. Low Temp. Phys. **1**, 215 (1975)].
[18]S. G. Akopov and Yu. E. Lozovik, Fiz. Nizk. Temp. **7**, 521 (1981) [Sov. J. Low Temp. Phys. **7**, 258 (1981)].
[19]G. Deutscher, Y. Imry, and L. Gunther, Phys. Rev. B **10**, 4598 (1974).
[20]V. L. Ginzburg, Fiz. Tverd. Tela (Leningrad) **2**, 2031 (1960) [Sov. Phys. Solid State **2**, 1824 (1961)].
[21]L. P. Kadanoff, W. Götze, D. Hamblen, R. Hecht, E. A. S. Lewis, V. V. Palciauskas, M. Rayl, J. Swift, D. Aspnes, and J. Kane, Rev. Mod. Phys. **39**, 395 (1967).
[22]D. H. Douglass and R. H. Blumberg, Phys, Rev. **127**, 2038 (1962).
[23]P. B. Miller, Phys. Rev. **113**, 1209 (1959).
[24]I. O. Kulik, Pis'ma Zh. Eksp. Teor. Fiz. **14**, 341 (1971) [JETP Lett. **14**, 228 (1971)].
[25]Yu. N. Ovchinnikov, Zh. Eksp. Teor. Fiz. **64**, 719 (1973) [Sov. Phys. JETP **37**, 366 (1973)].
[26]I. O. Kulik, Pis'ma Zh. Eksp. Teor. Fiz. **10**, 488 (1969) [JETP Lett. **10**, 313 (1969)].
[27]K. E. Gray and P. A. Bancel, in: Ordering in Two Dimensions (Proc. Intern. Conf., Lake Geneva, Visc. 1980, ed. by S. K. Sinha), North-Holland, Amsterdam (1980), p. 483.
[28]R. Kubo, J. Phys. Soc. Jpn. **17**, 975 (1962).
[29]Yu. F. Komnik, L. A. Yatsuk, V. V. Andrievskiĭ, K. K. Man'kovskiĭ, and V. V. Pilipenko, Fiz. Tverd. Tela (Leningrad) **13**, 1779 (1971) [Sov. Phys. Solid State **13**, 1486 (1971)].
[30]V. L. Ginzburg, Usp. Fiz. Nauk **95**, 91 (1968) [Contemp. Phys. **9**, 355 (1968)].
[31]J. W. Garland, K. H. Bennemann, and F. M. Mueller, Phys. Rev. Lett. **21**, 1315 (1968).
[32]R. Watton, J. Phys. C **2**, 1697 (1969).
[33]R. Watton, Solid State Commun. **8**, 105 (1970).

Translated by A. Tybulewicz