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## Manifestation of the proximity effects in tunnel conductance of multilayer systems

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An experimental investigation was made of the tunnel characteristics of thin films of "poorly conducting" substances, CuCl, Bi-Sb, and normal metals, Cu and Ag, covered by superconducting lead. These characteristics were determined in a wide temperature range (1-300°K) at pressures up to 17 kbar. The changes in the tunnel conductance of these systems were explained qualitatively within the framework of the familiar ideas of the proximity effect. It was found that a copper chloride film had semiconducting properties and did not go over to the metallic and superconducting state.

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### 1. INTRODUCTION

The electron spectrum of a conducting material undergoes considerable changes when this material is brought into contact with a superconductor. An investigation of this phenomenon, known as the proximity effect, is of fundamental importance for the understanding of the nature of superconductivity<sup>1</sup> and it makes it possible to determine various characteristics describing the properties of the electron and phonon subsystems of the investigated objects.<sup>2-4</sup> The extensive experimental data on the proximity effect have been obtained mainly for contacts of a normal metal with a superconductor.<sup>1</sup> It seems interesting and desirable to investigate multilayer structures with semimetals and semiconductors because of the possibility of superconductivity mechanisms other than the electron-phonon effect, particularly the exciton mechanism near a semiconductor-superconductor interface.<sup>5</sup> In this sense, there is definite interest in systems such as CuCl and Bi-Sb, in which a transition to a metallic and even superconducting state is possible at high pressures.<sup>6-8</sup>

We carried out tunnel experiments on thin films of CuCl (10-200 Å) and Bi-Sb (1000 Å), which were in direct contact with superconducting lead. A study was made of changes in the tunnel conductance because of the proximity of these relatively "poorly conducting"

substances with a superconductor, and because of the application of hydrostatic pressures up to 17 kbar.

We carried out additional experiments on normal metal-superconductor systems (Cu/Pb, Ag/Pb) composed of films of the same thickness as in the case of CuCl/Pb. In the majority of earlier investigations of these structures, attention was concentrated on the behavior of the tunnel conductance near the energy gap and the experiments were usually carried out on relatively thick ( $\geq 200$  Å) films of normal metals.<sup>1</sup> Having thus extended the investigated energy range, we shall consider the applicability of various models of the proximity effect to the tunnel characteristic as a whole in the range of energies corresponding to the superconducting gap as well as in the range of phonon excitations of the superconducting (lead) coating.

### 2. EXPERIMENTS

1. We investigated cross-shaped structures of the superconducting aluminum-aluminum oxide-investigated substance/lead (Al-I-N/Pb) type, prepared by thermal evaporation of the various substances in a vacuum of  $\sim 10^{-6}$  Torr. A tunnel barrier was formed by oxidation of aluminum in a dry oxygen atmosphere or in air for 5-15 min at a pressure of 0.3-0.5 Torr in the chamber. Alu-

minum films, 100 Å thick, were deposited on a substrate cooled to 77°K and were heated to 300°K before oxidation. The subsequent evaporation of a layer of *N* (CuCl, Bi-Sb, Cu, Ag) and of lead on the oxidized aluminum surface completed the preparation of the structures. The substrate was then cooled to 250 and 300°K for CuCl and Bi-Sb, respectively, to 80–100°K for Cu and Ag, and to 150–200°K for lead. Conventional technology<sup>9</sup> was employed in preparing a fine-grained powder of copper chloride which was the starting material in the formation of thin films.<sup>1)</sup> The thicknesses of the films forming a tunnel contact were determined with an MII-4 microinterferometer (thick films) and from the weight of the charge. Moreover, control measurements of the thickness were carried out with a standard quartz transducer of the KIT-2 type. In all these experiments, the thickness of the lead coating was 1500–2000 Å. The thickness of the layer *N* was determined to within 20%. The edge effects were eliminated by depositing all the films through masks held directly on the substrate by a small electromagnet. A batch of nine contacts of areas  $s \approx 0.03 \times 0.8$ ,  $0.6 \times 0.8$ , and  $0.8 \times 0.8$  mm was prepared simultaneously; these contacts were deposited on three glass substrates,  $4 \times 16$  mm. The probability of diffusion in the *N/S* layers was minimized by mounting the samples relatively rapidly (in 10–15 min) in a cryostat, where the temperature could be varied from 1 to 300°K. The extremely high resistances of the CuCl films at  $T \leq 77$ °K ( $10^5$ – $10^7$  Ω) made it impossible to carry out direct measurements on the Al-I-CuCl contacts; in the case of the Bi-Sb alloys, some of the experiments were carried out in the absence of lead.

The current-voltage *I-U* characteristics (with the current *I* and the voltage *U* in the energy units) and their derivatives were determined with a high-resolution spectrometer.<sup>10</sup> The degree of modulation needed to resolve those singularities in the  $dI/dU-U$  characteristics which were due to the energy gap of the semiconductor amounted to 1–5 μV; the phonon singularities in the  $dU/dI-U$  and  $d^2U/dI^2-U$  dependences were resolved by modulation amounting to 20–100 μV. The normal state was induced by a superconducting solenoid ( $H = 10$  kG). High pressures (up to 17 kbar) were established in a bomb filled with a kerosene-oil mixture,<sup>11</sup> in which two substrates with six samples were placed. The pressures were deduced from the shift of the critical temperature of superconducting indium.

2. The tunnel experiments on sandwiches containing CuCl were preceded by mastering of the technology of preparation of "free" copper chloride films<sup>2)</sup> and measurements of the resistance in a wide range of thicknesses (up to 5 μ), temperatures, and pressures. The main difficulty in the film preparation was associated with the possibility of decomposition of copper chloride in the course of thermal evaporation (which could result in the formation of basic  $Cu^{2+}$  salt,  $CuCl_2$ , or in the precipitation of pure copper). The quality of such "free" films was monitored by x-ray and ESR analyses.<sup>3)</sup> The x-ray measurements were carried out using  $Cu K_\alpha$  radiation in the "transmission" configuration. The strongest line of CuCl was recorded and a check was made of the angular intervals in which the strongest Cu and  $CuCl_2$

lines were expected. The maximum error in the intensity measurements was 1%. It was found that, within the limits of this method, the CuCl films did not differ from the original substance. A more accurate determination of the  $Cu^{2+}$  content was made using an ESR spectrometer with a sensitivity of  $10^{13}$  spins/Oe. The absence of the ESR signal confirmed the results of the x-ray analysis to the effect that there was no  $Cu^{2+}$  in the investigated films (within the limits of the experimental error.) Significant changes in the relevant spectra were observed only after prolonged storage (5–10 days) of the films under atmospheric conditions or after deposition of CuCl and Pb on warm substrates. Therefore, the above substrate temperature ensured in practice 80% yield of high-quality copper chloride films. Finally, the effects associated with the possible precipitation of pure copper were eliminated by investigating also the Cu/Pb and Ag/Pb systems with the same film thicknesses as in the CuCl/Pb sandwiches. The temperature dependences ( $T \sim 77$ – $300$ °K) of the resistivity of the CuCl films had a typical semiconducting nature with an activation energy of 60–100 meV; the conductivity at 300°K was  $dI/dU = 1-2 \times 10^{-2} \Omega^{-1} \cdot cm^{-1}$ . These values were quite different from the data for bulk samples.<sup>12</sup>

3. As pointed out earlier, certain experimental difficulties were encountered in the preparation of tunnel structures with copper chloride. The quality of the tunnel barriers was highly sensitive to the moisture content of the oxidizing medium. Attempts to investigate sandwiches of the CuCl/Sn, In type were unsuccessful because of the chemical activity of the CuCl. Therefore, we shall only give the results obtained for the samples satisfying the criteria used widely in tunnel investigations.<sup>13,14</sup>

Cooling to liquid nitrogen temperatures increased the contact resistances inversely proportionally to their areas and, when the lead went over to the superconducting state, the conductivity corresponding to  $U=0$  changed in the same way as in Al-I-Pb samples. The tunnel characteristics of the Al-I-CuCl/Pb junctions had clear singularities at  $U = \Delta_{N/S} \pm \Delta_{Al}$ . Since the contacts were prepared in vacuum attained by means of the conventional oil pumps, the tunnel spectra in the 100–500 meV range had singularities due to inelastic excitation of organic molecules in the tunnel barrier.<sup>15</sup> The location of the main lines in the spectra of the better samples were not affected by variation in the copper chloride film thickness and did not differ from those obtained for the Al-I-Pb structures. All this was evidence of the dominant role of the tunnel mechanism of the flow of the current in such complex systems. The junction resistances were  $R_T \approx 50$ – $1000$  Ω and, for the same preparation conditions, they obeyed the inequality  $R_T(CuCl/Pb) > R_T(Pb)$ .

The majority of the contacts with copper chloride was fairly stable at  $T = 300$ °K for several hours (and sometimes for two or three days) after preparation and could withstand one or two cycles of heating from helium to room temperature without change in properties. As a rule, the contact resistance increased with time in the same way as  $R_T$  clean junctions. There was a considerable deterioration in the tunnel characteristics after

prolonged storage (2–10 days) of the samples at room temperature: instabilities were observed during passage of the current and this was clearly due to the decomposition of the copper chloride film and associated chemical reactions.

Over 400 structures with CuCl were prepared and investigated under various conditions and of these 70 were tested in the temperature range 1–4.2°K. The results reported below for the normal metal/superconductor systems were obtained in experiments on 36 Al–I–Cu/Pb junctions and on 8 Al–I–Ag/Pb junctions.

There were no special difficulties in experiments on Al–I–BiSb/Pb contacts. The typical results reported below were obtained for 9 samples immediately after preparation. Prolonged “aging” at 300°K resulted in irreversible changes in the tunnel characteristics because of alloying and diffusion at the interface.

### 3. RESULTS

1. Al–I–CuCl/Pb system. A distinguishing feature of these structures was exhibited by the voltage dependences of the conductance (Fig. 1): at  $T=1-77^\circ\text{K}$ , there was a region with a considerable rise in resistance at energies exceeding the limit in the phonon spectrum of lead. The relative change in the resistance within this region and the values of the limiting energies were very sensitive to the film condensation conditions. This region appeared most clearly for the systems with the thinnest CuCl films (10–50 Å) at a lower limit of 60–150 meV and an upper limit 300–500 meV; the maximum change in the resistance was 3–7%. Pressures up to 12 kbar had practically no influence on this part of the tunnel characteristic. Similar dependences were observed earlier in the tunneling in  $p$ -type semiconductor films and were attributed to their energy band structure.<sup>16</sup> In the case of layer systems, this behavior could be due to spacecharge regions associated with states on the surface of copper chloride or due to strong distortions of the shape of the potential barrier.

Figure 2 shows changes in the characteristics of the Al–I–CuCl/Pb contacts on increase in the thickness of the copper chloride film in the case when both electrodes (aluminum and lead) were in the superconducting state. Hence, the energy gaps  $\Delta_{\text{CuCl/Pb}}$ , found even for the thinnest CuCl films, were considerably smaller than the gap for lead,  $\Delta_{\text{Pb}}=1.4$  meV, and varied relatively slowly with the thickness of the chloride: from 1.35 meV for  $d_{\text{CuCl}}=16$  Å to 1.32 meV for  $d_{\text{CuCl}}=180$  Å. There were considerable changes in the characteristics in the energy range  $U > \Delta_{\text{Al}} + \Delta_{\text{N/S}}$  (Fig. 3), which manifested the vibrational spectrum of lead: the amplitudes decreased<sup>4</sup> (especially for the longitudinal peak at  $\omega_1 \sim 8.5$  meV) and the phonon singularities shifted toward lower energies. The tunneling in Pb, covered with copper chloride (Al–I–Pb/CuCl and Al–I–Pb/CuCl/Pb) revealed no differences from pure lead. The film thicknesses were the same as in the case of Al–I–CuCl/Pb but considerably greater for CuCl (up to 600 Å) and for lead (300–1000 Å). When CuCl was replaced with NaCl (Al–I–NaCl/Pb), the characteristics were, up to 70 Å,

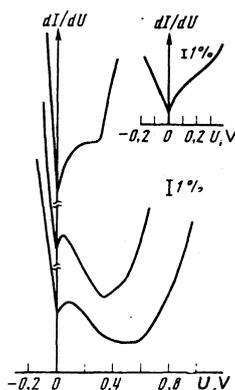


FIG. 1. Anomalous behavior of the tunnel conductance of three Al–I–CuCl/Pb structures subjected to high voltages across the barrier at  $T=77^\circ\text{K}$ . The inset shows the same dependence for an Al–I–Pb structure (here and later, the curves are copies of the experimental records).

again typical of the Al–I–Pb contacts. In the case of thicker NaCl films, there was a steep rise in the junction resistance up to  $10^4-10^5 \Omega$ . This was clearly associated with the fact that the thinnest CuCl (NaCl) films could be discontinuous, the tunnel currents could flow in parallel,<sup>17</sup> and special properties of copper chloride films could be manifested (insulating inclusions of NaCl did not participate in the tunneling).

Under hydrostatic pressures up to 12 kbar (2, 4, 8, and 12 kbar), the Al–I–CuCl/Pb samples exhibited no qualitative changes in the characteristics, which might have indicated a transition of the thin copper chloride film to the superconducting state. The shift of the main parameters (gap and phonon frequencies) was due to weakening of the electron–phonon interaction in the lead and was in agreement with earlier measurements on the Al–I–Pb contacts.<sup>18</sup> Measurements of the resistance of “free” CuCl films, 0.5–5  $\mu$  thick, carried out in a wide temperature (1–300°K) and pressure (up to 17 kbar)

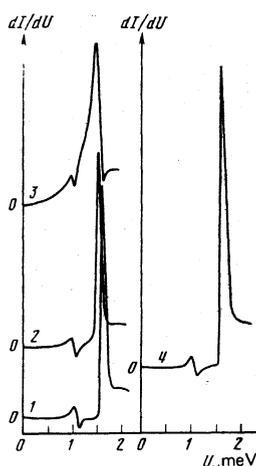


FIG. 2. Tunnel conductance of Al–I–CuCl/Pb structures in the energy range of the superconducting gaps of aluminum and lead with films of copper chloride of the following thickness  $d_{\text{CuCl}}$  (Å): 1) 16; 2) 65; 3) 180; 4) Al–I–Pb structure.  $T=1.1^\circ\text{K}$ .

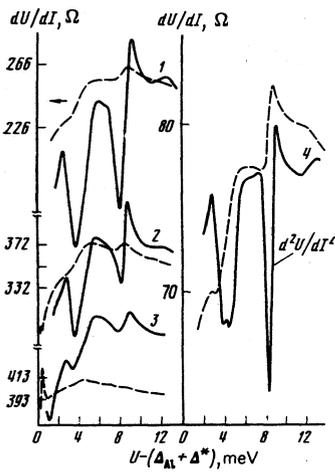


FIG. 3. Manifestation of phonon singularities of lead in the tunnel conductance of the same Al-I-CuCl/Pb structures as in Fig. 2, but at  $T=1.1$  °K. Here and later, the dashed curves represent the  $dU/dI-U$  dependences and the continuous curves are the  $d^2U/dI^2-U$  dependences. Here and in the remaining figures, the energies are measured from the sum of the gaps  $\Delta_{Al} + \Delta_{N/Pb} = \Delta_{Al} + \Delta$ .

range at various cooling and heating rates also showed no tendency for the conductance to increase.

2. Al-I-BiSb/Pb system (Fig. 4). As in the preceding case, the phonon structure of lead ( $U \geq 4$  meV) was considerably weakened but the positions of the characteristic frequencies ( $\sim 4$  meV and 8.5 meV) in the spectrum were hardly affected. The principal differences were found in the low-energy range ( $0 < U < 2$  meV) of the tunnel conductance. In addition to the clear peaks at  $U = \Delta_{N/S} + \Delta_{Al} = 1.7$  meV and  $U = \Delta_{N/S} - \Delta_{Al} = 1.1$  meV, the characteristic had an additional structure at  $U = 0-0.5$  meV, which could be attributed to the superconductivity induced in the BiSb film by lead. Pressures up to 12 kbar were applied to Al-I-Bi<sub>33</sub>Sb<sub>67</sub> contacts. Throughout this range, the characteristics were typical of the S-I-N systems (here, Al was a superconductor), which indicated the absence of the superconducting gap in the Bi-Sb system without a lead coating.

3. Al-I-Cu/Pb (-Ag/Pb) system (Fig. 5). In the case of small thicknesses of the N films (a, b), the singular-

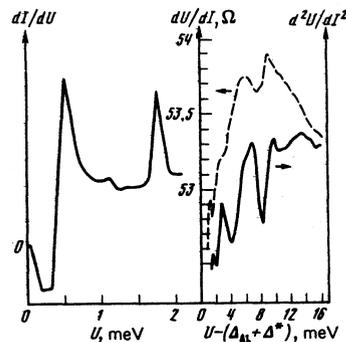


FIG. 4. Tunnel characteristics of Al-I-Bi<sub>33</sub>Sb<sub>67</sub>/Pb structures with  $d_{BiSb} = 1000$  Å at  $T=1.1$  °K.

ities at  $U = \Delta_{N/S} \pm \Delta_{Al}$  were clearly visible and similar to those exhibited by homogeneous superconductors. Samples of this system were characterized by the same gap with a smooth thickness dependence: 1.38 meV for  $d_N = 15$  Å and 1.27 meV for  $d_N = 50$  Å; there was also a considerable weakening of the amplitudes of the phonon singularities associated with longitudinal vibrations of the lead lattice ( $\omega_l \sim 8.5$  meV).

In the case of considerable thicknesses, there was a basic difference from the dependences  $dI/dU-U$  obtained for thin N films: as in the case of BiSb/Pb, two gaps were observed (c); the singularities near  $U = \Delta_{N/S} \pm \Delta_{Al}$  (d) became smeared out and the phonon structure of the lead became so distorted that it was close to the "inverted" form. In this case, the manifestation of the phonon spectrum of the lead in the tunnel conductance was basically similar to the results obtained for copper chloride (Fig. 3). In addition, judging by the change in the resistance in this range of energies ( $3$  meV  $< U < 10$  meV), CuCl had a greater influence on the tunneling into lead than did a layer of copper of the same thickness. Finally, all the systems exhibited an anomalous reduction in the conductance near  $U \geq \Delta_{N/S} + \Delta_{Al}$  (Figs. 2-5), which was not manifested by the Al-I-Pb contacts (curve 4 in Fig. 2).

Since, in these experiments, a study was made of the normal films of considerable thickness, whose tunnel characteristics were basically similar (in spite of the considerable differences between the properties of the investigated material), it seems appropriate to discuss the results obtained on the basis of the proximity effect.

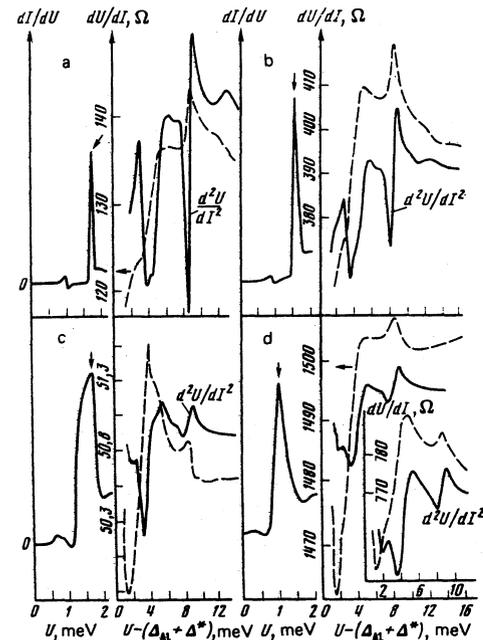


FIG. 5. Changes in the tunnel characteristics of Al-I-Cu/Pb systems with  $d_{Cu}$  (Å): a) 15; b) 50; c) 100; d) 200.  $T=1.1$  °K. The inset shows the characteristics of an Al-I-Ag/Pb structure with  $d_{Ag} = 150$  Å.

#### 4. DISCUSSION OF RESULTS

1. The contacts between a normal metal ( $N$ ) and a superconductor ( $S$ ) have been considered so far.<sup>1</sup> It has been shown that the probability of detection of Cooper pairs in an  $N$  film decreases exponentially away from the  $N/S$  interface and that the characteristic depth of penetration of these pairs is

$$\xi_N(T) = (\hbar v_N l_N / 6\pi kT)^{1/2}, \quad (1)$$

where  $v_N$  is the Fermi velocity,  $l_N$  is the mean free path, and  $T$  is the absolute temperature. It is of fundamental importance to note the existence on the  $N/S$  interface of a jump in the order parameter  $\Delta_0$ , whose value is governed by the difference between the electron-phonon interaction parameters of the  $N$  and  $S$  films.

We shall consider the influence of an  $N$  film on the tunnel density of states in a superconductor:<sup>14</sup>  $N_T^{(S)}(\omega) = \text{Re}\{\omega/\sqrt{\omega^2 - \Delta^2(\omega)}\}$ . We are interested in the range of characteristic phonon frequencies of lead  $\bar{\omega} = 3-10$  meV  $\gg |\Delta(\bar{\omega})|$ , where the density is

$$N_T^{(S)}(\omega) = 1 + \text{Re}\left\{\frac{\Delta_{pb}^2(\omega)}{2\omega^2}\right\}. \quad (2)$$

Computational difficulties associated with allowance for the spatial dependence of  $\Delta_0$  are usually avoided by assuming that the order parameter is constant but different in the  $N$  and  $S$  films forming a single contact. It is found that in this case the function  $N_T(\omega)$  can be represented by the following general expression:

$$N_T^{(N/S)}(\omega) = 1 + \text{Re}\left\{\frac{\Delta_{pb}^2(\omega)}{2\omega^2} F(\omega)\right\}. \quad (3)$$

In fact, Eq. (3) represents the usual tunnel characteristics of superconducting lead (2), modulated by the function  $F(\omega)$ .

In the model of Ref. 2, the  $N$  and  $S$  films are in direct contact and the  $N$  film has no energy gap. The resultant perturbation of the potential is responsible for the Andreev reflection from the  $N/S$  interface and appearance of interference effects in the density of states of the normal metal. When the energy of a tunneling electron is less than the superconductor gap, discrete levels may be observed<sup>19</sup> and if  $\omega \gg |\Delta(\omega)|$ , Eq. (3) has the following function

$$F_1(\omega) = \exp\left(-\frac{2d_N}{l_N}\right) \int_0^{\infty} \exp\left(i\frac{4\omega d_N x}{\hbar v_N}\right) \frac{dx}{x^2}. \quad (4)$$

Equations (3) and (4) were used to calculate the second derivatives of the tunnel current with respect to the voltage for thin  $N$  films (Fig. 6); use was made of the parameter  $\Delta_{pb}(\omega)$ , obtained from the tunneling into pure lead.<sup>10</sup> These calculations can be compared qualitatively with the experimental curves in Fig. 5. Attenuation of the amplitudes in the phonon structure of lead (Figs. 5a and 5b) and the tendency to "inversion" are due to a reduction in the period of the function  $F_1(\omega)$  on increase in thickness  $d_N$ . The applicability of this model to sandwiches with such thin  $N$  films is surprising and it is clearly due to the existence of a jump  $\Delta_0$  at the  $N/S$  interface, the detailed structure of this jump being unimportant in the  $\omega \gg \Delta_0$  case.

Nevertheless, the assumption  $\Delta_N(\omega) = 0$  is in conflict

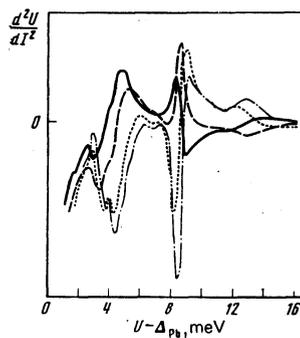


FIG. 6. Manifestation of the phonon structure of lead in the  $d^2U/dI^2-U$  dependences of the second derivatives. The calculations are carried out in the model of Ref. 2 for  $v_N = 1 \times 10^8$  cm/sec and  $d_N$ : the chain curve corresponds to 30 Å, the dotted curve to 100 Å, the dashed curve to 300 Å, and the continuous curve to 500 Å. Similar behavior is predicted by the model of Ref. 20 with  $\Gamma = 25, 15, 5,$  and 2 meV.

with the experimental data obtained in the low-energy range ( $\omega \sim \Delta_0$ ) for metal-superconductor contacts: a strong dependence of  $\Delta_{N/N}$  on the thickness and the appearance of two gaps indicate that superconductivity has been induced in the  $N$  film.

The behavior of the tunnel characteristics near the energy gap can be understood within the framework of the tunnel model with a potential barrier between the  $N$  and  $S$  films.<sup>20</sup>

The initial relationships between the self-energy terms of two metals in contact are given for this model in Ref. 4. If we assume that the electron-phonon gap coupling in the  $N$  film is very weak and that the ratio of the thicknesses  $d_S/d_N$  is large (i.e.,  $\gamma \gg 1$  in Ref. 4), we find from Eqs. (4) and (5) of Ref. 4 the relationship between  $\Delta_N(\omega)$  and  $\Delta_S(\omega)$  and it then follows that Eq. (3) is valid if

$$F_2(\omega) = -\frac{\Gamma^2(\omega - i\Gamma)^2}{(\omega^2 + \Gamma^2)^2}. \quad (5)$$

Here,  $\Gamma = \pi |T|^2 d_S n_s$ ;  $T$  is the tunnel matrix element allowing for the transfer of excitation from one electrode of an  $N/S$  contact to the other;  $s$  is the contact area;  $n_s$  is the density of states on the Fermi surface of the lead electrode.

It follows from Eq. (5) that, if  $\Gamma \ll \omega$ , the tunnel characteristics of the systems are "inverted" relative to clean (free of the  $N$  film) contacts [see Eq. (2)]. The reverse inequality results in an "uninverted" phonon structure of lead so that, in the limit  $\Gamma \gg \bar{\omega}$ , we obtain the "Cooper" case (see Ref. 4). Numerical calculations indicate that, for  $\Gamma \sim \bar{\omega}$ , the  $d^2U/dI^2-U$  dependences are very similar to the curves in Fig. 6. This is due to the fact that the function (4) and (5) behave similarly in this range of parameters when  $\omega \sim \bar{\omega}$ . Consequently, the dependences in Fig. 6 correspond qualitatively to the tunnel model with  $\Gamma \approx 25, 15, 5,$  and 2 meV. It should be stressed that this model postulates the existence of two gaps ( $\Delta_N \neq 0$  and  $\Delta_S$ ), which are responsible for the observed singularities in the tunnel characteristic. A change in the barrier transparency (i.e., in the interaction between the  $N$  and  $S$  films) results, within the

framework of this model, in considerable distortions of the measured dependences. Thus, the tunnel model is applicable to the case shown in Fig. 5c. We have to assume a low transparency of the resultant barrier at the Cu/Pb interface. The results in Fig. 5d can be analyzed on the assumption of tunnel transparency much stronger than that in Fig. 5c. On the whole, the tunnel model permits us to explain qualitatively all the observed changes in the tunnel conductance. However, in some cases (Figs. 5a and 5b), we cannot exclude the possibility of the validity of the model of Ref. 2.

2. We shall now consider the experimental results on the CuCl/Pb system. A single  $\Delta_{N/S}$  gap, somewhat smaller than that for pure lead, is due to the fact that the value of  $\Delta_0$  of lead at the interface decreases compared with its depth in the interior of the S film, whereas there is practically no superconductivity in the semiconductor film. We may assume that we have here the case close to the model of Ref. 2 with a jump in the gap at the N/S interface. This is not in conflict with the observed manifestation of the phonon excitations of lead (Fig. 3).<sup>5</sup> None of the samples behaves analogously to the "metallic" conduction near  $U = \Delta_{Pb} \pm \Delta_{Al}$  (absence of two gaps and strong dependence of  $\Delta_0$  on the thickness of the copper chloride). Consequently, the CuCl film is practically in the normal state (with the possible exception of an extremely thin boundary layer,  $\sim 5-10 \text{ \AA}$ ). According to Eq. (1), the penetration of superconducting electrons to such a small depth is due to their low velocity and short mean free path. This is also supported by the data on the tunneling into a thin Pb film coated with CuCl.

We attempted to reconstruct<sup>21</sup> the electron-phonon interaction  $g_{CuCl/Pb}(\omega)$  for  $d_N = 16 \text{ \AA}$  and, in contrast to  $g_{Cu/Pb}(\omega)$  for  $d_N = 15 \text{ \AA}$ , we obtained nonphysical parameters  $\mu^* < 0$  and  $\lambda \sim 1$ . This indicated the absence of the "Cooper" case even for such thin copper chloride films.<sup>4</sup>

Finally, the behavior of the characteristics of the BiSb/Pb sandwiches (Fig. 4) can be understood within the framework of the tunnel model of the interaction between the BiSb and Pb films. The appearance of singularities at low voltages across the barrier is due to the superconductivity induced in BiSb and characterized by  $\Delta_0 \leq 0.1 \text{ meV}$  (such characteristics have already been observed in metal contacts with artificial barriers<sup>22</sup>). In spite of the considerable thickness of the N films ( $\sim 1000 \text{ \AA}$ ), none of the samples exhibits size effects of the type discussed in Ref. 2 [see also Eq. (5)]. This is due to the fact that the semimetal-metal interface prevents the Andreev reflection.

It is premature to consider a quantitative comparison of the experiment with theory because the structure of the surface depends on the conditions during film deposition and each interface has its own properties. This is indicated by the presence of surface states and is clearly reflected in the scatter of the absolute values of  $\Delta_{N/S}$  and ratios of the tunnel conductivity  $\sigma_S/\sigma_N(U=0) = 0.05-0.003$  at the temperature of our experiments. Moreover, we cannot exclude the possibility of the presence of inhomogeneities and pores in the N films. How-

ever, these factors are of no importance in a qualitative discussion.

## 5. CONCLUSIONS

The observed changes in the tunnel conductance of the Al-I-CuCl/Pb and Al-I-BiSb/Pb systems can be understood qualitatively by applying the familiar ideas on the proximity effect, which have been developed for metallic systems. Application of the tunnel model<sup>20</sup> and numerical analysis of the reflection of the phonon spectrum of a superconducting coating on an N film show that, for a certain transparency of the barrier between the N and S films ( $\Gamma \sim \bar{\omega}$ ), the results are close to those obtained from the interference model.<sup>2</sup> There is at present no detailed quantitative theory allowing for the spatial variation of the superconducting parameter of the energy gap in layer structures. Therefore, we face the problem of selection of a model describing adequately the proximity effect and of considerable complication of the procedure of finding the functions  $g_N(\omega)$  and  $g_S(\omega)$  for the materials in contact. In view of the faster (than in metals) decay of superconducting wave functions inside a semiconductor (semimetal), we can justifiably neglect the dependence  $\Delta(r)$  and, therefore, the situation may be more favorable for a qualitative analysis of the tunneling in multilayer systems containing a semiconductor or semimetal. However, in the experimental studies, we still have the complication of the formation of a defect-free interface close to that considered in theoretical models.

The tunnel and resistance measurements indicate that thin copper chloride films (prepared by the available technology) have semiconducting properties and do not go over to the metallic and superconducting state at  $T = 1-300^\circ\text{K}$  at hydrostatic pressures up to 17 kbar. Under the same conditions, films of the Bi-Sb alloys also do not become superconducting. However, a tunnel study of the energy gap induced by superconducting lead shows that the interaction parameter in these alloys corresponds to attraction and, therefore, it may be possible to detect superconductivity under other conditions (concentrations, temperatures, and pressures). Finally, a strong influence of thin CuCl films on the tunnel conductance at energies corresponding to the inelastic excitation of intrabarrier organic molecules (100-500 meV) is observed. This influence is associated with the nature of the potential barrier and detailed experimental investigations will be continued.

On the theoretical side, allowance has to be made not only for one-particle tunneling within the tunnel model but also for the transfer of coupled electron pairs from one superconducting film to another (Josephson tunneling). Moreover, in the proximity effect, we can expect changes not only in the superconducting properties but also in the normal characteristics of metals which are brought into direct contact.

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- <sup>2</sup>Films of different widths (0.01–0.8 mm) and lengths (0.01–15 mm) were deposited on glass substrates with gold contacts (planar configuration of the Au–CuCl–Au bridge type).
- <sup>3</sup>The authors are grateful to S. D. Vangengeĭm and V. A. Sil'chenko for considerable help in these analyses.
- <sup>4</sup>The resistance scale for  $dU/dI-U$  can be used to estimate quite easily the changes in the amplitudes of the phonon singularities.
- <sup>5</sup>The distortion of the  $dI/dU-U$  characteristic near  $U=\Delta_N/s \pm \Delta_{A1}$  for  $d_N \approx 200 \text{ \AA}$  is possibly due to the appearance of states inside the gap.<sup>1</sup>
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## Effect of local flattenings of the Fermi surface on the absorption and dispersion of sound

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It is shown that the zero-curvature points and lines result in a sharp dependence of the absorption and velocity dispersion of sound on the direction of propagation. The nature of this dependence is determined by the shape of the local flattening and its orientation with respect to the principal directions. In contrast to ordinary absorption and dispersion, the contribution of the zero-curvature points and lines depends at  $k/\nu > 1$  on the frequency and the temperature. The presence of zero-curvature lines on the Fermi surface also leads to a change in the angular dependence of the absorption and dispersion in a strong magnetic field and to anisotropy of the tilt effect.

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As is well known,<sup>1,2</sup> a transition from viscous low-frequency absorption  $\gamma/\omega \sim \omega/\nu$  to collisionless absorption  $\gamma/\omega \sim s/\nu$  takes place in pure metals at low temperatures with increase in the sound frequency. In col-

lisionless absorption, only the electrons of a narrow "belt"  $\mathbf{k} \cdot \mathbf{v} = \omega$  take part; these electrons are in synchronism with the sound wave; therefore the absorption is usually little sensitive to the geometry of the Fermi