SUPERCONDUCTIVITY

Localized superconducting pairs

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Various phenomena which aid in understanding the concept of localized superconducting pairs (the behavior of granular superconductors, the parity effect, the Berezinski–Kosterlitz–Thouless transition) are discussed. Experimental evidence of the existence of localized pairs is presented and the conditions favoring their appearance are analyzed. © *2011 American Institute of Physics*. [doi:10.1063/1.3551532]

The notion that a superconducting interaction can support the dissipationless flow of current through a metal but also facilitate localization and lead to the formation of an insulating state seems paradoxical and has been accepted only with difficulty. This paper is a comprehensive discussion of the model of localized superconducting pairs which lies at the center of that notion. The model provides a concrete representation of the idea of a Bose insulator or Bose glass, first proposed in a study[1] of Bose-Einstein condensation in a charged Bose gas in the field of charged impurities and then developed in detail[2] in an examination of phase transitions in a system of bosons with weak repulsion located at lattice sites.

The article begins with definitions and general notation. This is followed by a short description of zero-dimensional superconductivity in individual grains and the behavior of an ensemble of such grains in a granular superconductor, as well as of the parity effect in an isolated small grain. This is one logical way of interpreting the concept of localized pairs, from granules to point defects.

There is another logical path, namely: a superconductor is a dissipative medium with an equilibrium concentration of Cooper pairs—an insulator with localized pairs. This kind of approach is suggested, first of all, by the Berezinski–Kosterlitz–Thouless (BKT) transition, where there is an equilibrium concentration of Cooper pairs on both sides of the transition of the metal into a dissipationless state. Second, besides the main Bardeen–Cooper–Schrieffer (BCS) model for superconductivity, there is a model which treats a superconducting transition as Bose-Einstein condensation (BEC). The use of this model or some modification of it[3] is justified, at least, for low electron concentrations. The BEC model also contains electron pairs (bosons), and they exist on both sides of the BEC point. And finally, this approach is simpler. Once it is assumed that uncorrelated electron pairs can exist in a dissipative medium, it is natural to assume that they may be localized.

These digressions should help the reader accept the experimental proofs of the existence of localized pairs presented in section IV of this paper: negative magnetoresistance on the insulator side in the neighborhood of the superconductor-insulator transition, the first measurements of the density of states near the Fermi level in this insulator, and the first successful attempts at a direct measurement of the effective volume of a localized pair. Then factors which facilitate pair localization are discussed: the distinctive statistical properties of the random potential resulting from the chemical composition of the material, and the closeness of the insulator-normal metal transition.

This paper relies on a recently published review[4] dealing with superconductor-insulator transitions.

I. INTRODUCTION

We refer to an electron localized on a defect or center as localized when its wave function is damped exponentially at large distances r from the defect, i.e.,

$$\psi = \psi_0 \exp(-r/\Lambda), \quad r \gg \Lambda, \tag{1}$$

where Λ denotes the localization length. For an isolated defect the localization length is usually identified as the Bohr radius and denoted by a_B. Since localization takes place against the background of a random potential, the energies of the electrons at all the centers differ slightly. However, for a finite temperature $T \neq 0$, an electron can hop from one center to another, conserving energy as a result of accompanying processes, such as emission or absorption a photon. These electron hops make jump conductivity possible. At low temperatures a jump conductivity σ_k of the form

$$\sigma_h = \sigma_{h0} \exp[-(T_1/T)^{1/\nu}], \quad \nu = 1,2,3 \text{ and } 4; \tag{2}$$

usually occurs, where the particular value of ν depends on the type of jump conductivity, the density of states $g(\varepsilon)$ near the Fermi level ε_F, and the dimensionality.

When the exponential tails of the wave functions of electrons localized at different defects overlap, the localization length increases and becomes greater than a_B. In particular, this sort of overlap is always observed on approaching an insulator-metal transition. As the transition is approached the localization length Λ increases and right at the transition it goes to infinity, so that

$$a_B \leqslant \Lambda \leqslant \infty. \tag{3}$$

The interaction between localized electrons does not, in general, lead to overlap of their wave functions. In particular, it is possible to imagine that an additional superconducting interaction takes place between two such electrons, i.e., that they exchange virtual phonons so that the energy of both of them decreases by Δ_L. Exchange requires that the separation between the energy levels of an electron, determined by its localized volume, be less than the energy of the phonons. If such an interaction actually occurs, then it is possible to introduce a wave function for a localized electron pair. It also damps out exponentially at large distances,

$$\psi_2 = \psi_{20} \exp(-r/\Lambda_2), \quad r \gg \Lambda_2, \tag{4}$$

with a characteristic length Λ_2 for which an inequality similar to Eq. (3) applies in the neighborhood of an insulator-superconductor transition:

$$a_{2B} \leqslant \Lambda_2 \leqslant \infty. \tag{5}$$

Jump conductivity is also possible in an insulator with paired electrons. However, one of the following two things must happen. On one hand, both electrons can hop to new centers simultaneously, and remain bound; this process is little studied, although it may occur immediately adjacent to a superconductor-insulator transition. We return to this case below. On the other hand, as one of the electrons jumps, it "pays off" its partner, leaving it an additional energy Δ_L. The contribution to the conductivity from this type of jump with unpairing includes an additional small factor

$$\Delta\sigma_h^{(2)} \sim \Delta\sigma_h \exp(-\Delta_L/T). \tag{6}$$

In any case, it is to be expected that the activation conductivity of an insulator I_2 with paired carriers is less than for an ordinary insulator.

The purpose of this paper is to clarify just how realistic such a localized pair model is and to examine experimental data which can be regarded as proof of the existence of localized pairs.

II. GRANULAR SYSTEMS

A. Pseudolocalization of Cooper pairs in a granular metal

Let us consider a material consisting of grains of superconducting material in an insulating matrix. Assume the average grain size b is such that the ratio

$$\Delta/\delta\varepsilon = \Delta g_F b^3 \gg 1, \tag{7}$$

where Δ is the superconducting gap, $\delta\varepsilon = (g_F b^3)^{-1}$ is the separation between electron levels owing to size quantization, and g_F is the density of states at the Fermi level of the bulk metal in its normal state. It is, in fact, the presence of the gap Δ in a relatively dense system of electronic levels which allows us to refer to such a granule as superconducting. The quantity on the left of this inequality can be interpreted as a requirement that the number of Cooper pairs in each granule be large, i.e.,

$$(g_F\Delta)b^3 \gg 1. \tag{8}$$

The superconducting state of a grain is a collective state of all the Cooper pairs. It is described, as in a bulk superconductor, by the complex order parameter

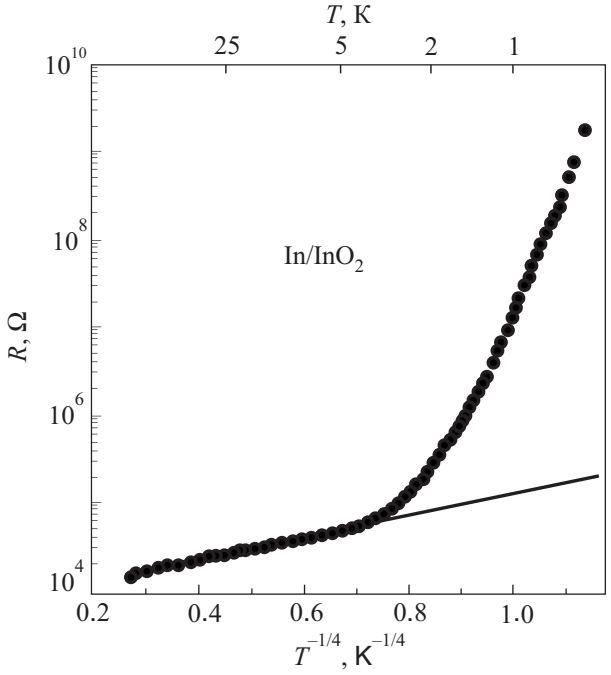

FIG. 1. Temperature dependence of the resistance of granular film consisting of grains of In separated by oxide.[5] This manifests the characteristic increase in resistance below the superconducting transition temperature of the indium grains.

$$\Phi(\mathbf{r}) = |\Phi| \exp(i\varphi(\mathbf{r})), \tag{9}$$

whose modulus is the binding energy of a Cooper pair, i.e., $|\Phi| = \Delta$, and whose phase $\varphi(\mathbf{r})$ characterizes the coherence of the Cooper pairs. When there is no current in the superconductor, $\varphi(\mathbf{r}) = \text{const}$.

Charge transfer from one grain to another is possible only by tunnelling. If this charge transfer were by Josephson currents of Cooper pairs, then the phase of the order parameters in all the grains would be correlated and a macroscopic superconducting state would be established in the material. Josephson currents, however, can be suppressed by, for example, an excessively high normal tunnel resistance between the granules, $\rho \gg \hbar/e^2$. Then charge transfer between grains occurs through tunnelling of single particle excitations, whose density n_1 is exponentially small in the grains because of the superconducting gap Δ, i.e.,

$$n_1 \propto \exp(-\Delta/T). \tag{10}$$

Under these conditions superconductivity is established in each grain independently. It can be said that the pairs are localized, each within its grain, and the radius of localization Λ is equal to the grain size b, i.e.,

$$\Lambda_2 = b.$$

If the grain size b if macroscopic and condition (8) is satisfied, then this interpretation is not completely consistent with the ordinary meaning of the word "localization." First, the proposed interpretation shows that the idea of localized superconducting pairs is not as crazy as it seemed at the start. Second, it encourages a close scrutiny of the transport properties of high resistance granular superconductors. These properties are illustrated in Fig. 1, where the resistance R of a granular In/InO system is plotted as a function of tempera-

ture. For temperatures T above the superconducting transition temperature T_c of indium, the resistance $R \equiv R_n$ increases with decreasing temperature in accordance with the Mott law, as in an ordinary insulator. The $R(T)$ curve is certainly sensitive to the superconducting transition, but below T_c the resistance $R \equiv R_{sc}$ does not decrease, but instead, increases much more rapidly.

This effect is qualitatively fully understandable. On top of the ordinary processes controlling the resistance of an insulator at finite temperatures, here the single particle excitations in the granules which are capable of tunnelling become frozen as implied by Eq. (10). This introduces an additional factor in the expression for R_{SC},

$$R_{sc} = R_n \exp(\Delta/T).$$

If a magnetic field is used to destroy the superconducting gap in the granules so they become normal, then the number of single particle excitations at the Fermi level will increase and the resistance returns to R_n. This indicates the presence of a negative magnetoresistance, which is stronger for lower temperatures, i.e.,

$$R(B,T)/R(0,T) \approx \exp(-\Delta/T), \quad B > B_c, \tag{11}$$

where B_c is the critical magnetic field.

In general, all of these remarks could be applied to hypothetical localized pairs in a quasi-inhomogeneous material once the word "tunnelling" is replaced by "hopping" and the magnetic field is assumed to destroy the pairwise superconducting correlations in the localized pairs. If the localized pairs inherit the singlet character of the Cooper pairs and the two electrons from a pair have opposite spin directions, then a magnetic field, which tends to align all the spins in one direction, will reduce the energy gain from pairing and a sufficiently high field will reduce it to zero. Of course, the notion of localized pairs' reacting in this way to a magnetic field requires experimental verification. In any case, *experiments on granular superconductors indicate a possible experimental approach to search for electron pair localization. If electron pairs localized on local defects do exist, then in a strong magnetic field we should expect a negative magnetoresistance owing to breakup of these pairs*.

B. Parity effect in small grains

A parity effect has been observed[6,7] in superconducting grains with sizes satisfying condition (7) using Coulomb blockade. Adding one additional odd electron to the electron system increased the total electron energy E_N more than adding the next odd electron. The difference was equal to $2\Delta_p$, where

$$\Delta_p = E_{2l+1} - \frac{1}{2}(E_{2l} + E_{2l+2}) \tag{12}$$

is the binding energy per electron. In a large grain, $\Delta_p = \Delta$.

If the grain size is reduced, then, because of the breakdown of condition (7), superconductivity should vanish. This happens when $b < b_1$, where b_1 is determined by comparing the superconducting gap Δ to the distance $\delta\varepsilon$,

$$\delta\varepsilon = (g_F b_1^3)^{-1} = \Delta, \quad b_1 = (g_F \Delta)^{-1/3}. \tag{13}$$

However, the superconducting interaction through phonons remains and, as before, leads to an effective attraction between electrons. Besides this, it ha been shown theoretically[8] that the parity effect also remains. The binding energy Δ_p in small grains[8] with

$$b \ll b_1, \text{ i.e. } \delta\varepsilon \gg \Delta, \tag{14}$$

becomes a small correction relative to $\delta\varepsilon$, but it is not at all small relative to the gap Δ in the bulk material, i.e.,

$$\Delta_p = \frac{\delta\varepsilon}{2\ln(\delta\varepsilon/\Delta)} > \Delta. \tag{15}$$

This analysis[8] is valid as long as size quantization is smaller than the energy of a Debye phonon $\hbar\omega_D$. This means that there is a *range of sizes of isolated grains of superconducting metal*

$$b_2 \ll b \ll b_1,$$

$$b_2 = (g_F \hbar\omega_D)^{-1/3}, \quad b_2/b_1 \approx (\Delta/\hbar\omega_D)^{1/3}, \tag{16}$$

within which the superconducting interaction can lead to pairing of electrons localized inside a grain over a length b.

III. DELOCALIZED ELECTRON PAIRS IN DISSIPATIVE MEDIA

According to the classical BCS theory of superconductivity, an equilibrium concentration of Cooper pairs appears at the temperature T_c simultaneously with the establishment of a dissipationless state, which we shall regard as intrinsically superconducting. Superconductivity is usually destroyed by bringing the modulus of the order parameter $|\Phi| \equiv \Delta$ to zero by, for example, raising the temperature to T_c or the critical field to B_c. In this section we shall be interested in the possibility of the separate onset of two events: the destruction of the superconducting state and the approach of $|\Phi|$ to zero, i.e., the possibility of dissipation with a nonzero equilibrium concentration of electron pairs. We examine two such cases.

A. The Berezinski-Kosterlitz-Thouless transition

Two-dimensional superconducting systems are distinguished by the possible existence of a gas of fluctuations in the form of spontaneously generated magnetic vortices below the bulk superconducting transition temperature T_{c0}. Each vortex is penetrated by a quantum of magnetic flux

$$\Phi_0 = 2\pi\hbar c/2e. \tag{17}$$

The vortices are created in pairs with opposite directions of the on-axis field (vortex-antivortex pairs) and after a finite time, they are annihilated in collisions. In zero magnetic field the concentrations of the vortices with opposite signs are equal, i.e., $N_+ = N_-$, and are determined by the dynamic equilibrium between spontaneous creation and annihilation processes. A transit around a motionless vortex changes the phase of the wave function by 2π, so that free movement of the vortices leads to fluctuations in the phase. If the amplitude of the fluctuations in the phase is sufficiently high, the coherence of the state is lost. Here the modulus of the order

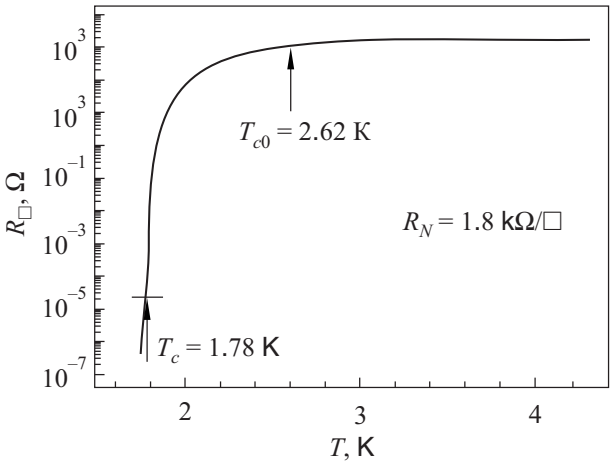

FIG. 2. The temperature T_{c0} at which an equilibrium concentration of Cooper pairs occurs and the temperature T_c at which a coherent state forms in a 100-Å-thick amorphous In–O film.

parameter Δ remains nonzero over a larger part of the volume. (It goes to zero only inside vortices, near the vortex axis.)

As the temperature is lowered, at some $T<T_{c0}$ a BKT transition takes place:[9,10] creation of vortex pairs ceases, and the vortex concentration falls off sharply, becoming exponentially small. In addition, the dissipation also becomes exponentially small only for $T<T_c$. But within some range of temperatures

$$T_c < T < T_{c0} \tag{18}$$

Cooper pairs coexist with vortices in two-dimensional superconductors. The Cooper pairs reduce the dissipation, but do not suppress it completely.

Mathematically the existence of a dissipationless state means that at large distances the correlator

$$G(r) = \langle \Phi(r)\Phi(0) \rangle \to G_0 \neq 0, \quad \text{for } |r| \to \infty \tag{19}$$

remain finite (the angular brackets denote averaging over the quantum state of the system). In the temperature range (18) the correlator (19) goes (exponentially) to zero with increasing r. For temperatures $T<T_c$ it falls according to a power law, i.e., it still approaches $G_0=0$ at large distances, but relatively slowly. Thus, in the temperature range (18) a dissipative state develops in a two-dimensional superconductor and for $T<T_c$, an almost coherent state. A strictly coherent state with a finite correlator (19) at large distances develops in two-dimensional systems only at $T=0$.

An example of determining the temperatures T_{c0} and T_c using the resistive transition is shown in Fig. 2. A detailed experimental analysis[11] based on theoretical calculations[12] has been carried out for the superconducting transition in amorphous In–O films.

According to the figure, the temperatures T_{c0} and T_c differ by almost a factor of 1.5: that is, $R(T_{c0}) \approx 0.5R_N$, and $R(T_c)$ is less than R_N (the resistance of the film in the normal state) by several orders of magnitude.

B. Superconductivity as Bose condensation

The BCS theory assumes that the coherence length (size of a Cooper pair) $\zeta \sim \hbar v_F/\Delta \sim 10^{-4}$ cm is considerably greater than the average distance between pairs, $s \sim (g_0\Delta)^{-1/3} \sim 10^{-6}$ cm (g_0 is the density of states in the normal metal at the Fermi level), i.e.,

$$\zeta \gg s. \tag{20}$$

Essentially a collective state of all the electrons in the form of ensemble of Cooper pairs is considered.

However, superconductivity also develops in systems with electron densities considerably lower than in ordinary metals, such as, single crystal $SrTiO_3$ with an electron density on the order of $n \sim 10^{19}$ cm^{-3}.[13] Furthermore, in type II superconductors the parameters ζ can be less than 100 Å. Thus, the inequality (20), which is necessary for validity of the BCS model, may be violated. Materials in which $\zeta \lesssim s$ are among the exotic superconductors.

The existence of exotic superconductors, for which the inequality (20) does not hold, has led to another model of superconductivity—Bose–Einstein condensation of a gas of electron pairs treated as bosons with charge 2e[14]—and to studies of crossover from the BCS model to the BEC model.[3]

The BEC model assumes another way of destroying the superconducting state: fluctuations in the phase of the order parameter drive the correlator (19) to zero when the modulus of the order parameter is nonzero.[15] A finite modulus of the order parameter at the transition signifies a finite concentration of bound electron pairs, i.e., the boson concentration does not go to zero at the transition. This sort of scenario is made more likely by the fact that shielding is weaker and the "rigidity" with respect to phase changes is comparatively small (which increases the role of phase fluctuations) in superconductors with a low electron density.[16,17]

While assuming that bosons (electron pairs) are present on both sides of the superconducting transition, the BEC model does not discuss the mechanism for their appearance above T_c. It may be supposed, for example, that they show up independently of one another owing to a Cooper interaction and their relative amount is determined by the Boltzmann factor $\exp(-\Delta/T)$. At higher temperatures $T \gg \Delta$ their number becomes exponentially small.

Once the existence of uncorrelated electron pairs in a dissipative medium is recognized, the question of whether these pairs are localized becomes completely natural and the answer depends on the level of disorder. An equilibrium concentration of electron pairs implies the existence of a gap or, at least, a minimum in the density of single-particle states of the electron system at the Fermi level. *Measuring the density of states on both sides of the superconducting transition and searching for a minimum at the Fermi level on the nonsuperconducting side are possible topics for experimental research.*

IV. EXPERIMENTAL EVIDENCE OF THE EXISTENCE OF LOCALIZED PAIRS

In the preceding sections we have determined two possible types of experiments for detecting localized pairs in uniformly disordered materials. The existing experimental data are reviewed in this section.

A. Negative magnetoresistance

It is most natural to search for localized pairs in materials which become highly resistive after a breakdown of superconductivity, that is, in the neighborhood of a superconductor-insulator transition. We shall speak of two groups of materials of this sort: ultrathin films whose thickness b serves as a controlling parameter (superconducting for large b and insulating for small b) and materials with a variable composition that can be controlled in some way. In the second group the controlling parameter is usually the electron concentration and/or the level of disorder. In both groups, a magnetic field B can be used as a control parameter.

Let us examine in more detail the possible consequences for electron transport of field-induced destruction of localized pairs. First, the binding energy has dispersion: it depends on the specific values of the random potential in the neighborhood of the localization point $\mathbf{r}_i$, as does the energy $\varepsilon^{(1)}$ of this electron when the pairwise superconducting interaction is shut off:

$$\varepsilon(\mathbf{r}_i) = \varepsilon^{(1)}(\mathbf{r}_i) - \Delta_L(\mathbf{r}_i). \tag{21}$$

By definition $\varepsilon(\mathbf{r}_i) < \varepsilon_F$. However, $\varepsilon^{(1)}(\mathbf{r}_i)$ can be either smaller or greater than ε_F. In the first case, $\varepsilon^{(1)}(\mathbf{r}_i) < \varepsilon_F$, after destruction of the pairwise correlations by the field and Δ_L goes to zero, an electron remains localized at the point $\mathbf{r}_i$. Its contribution to the conductivity increases according to Eq. (6), but the conductivity is still jump conductivity. In the second case, $\varepsilon^{(1)}(\mathbf{r}_i) > \varepsilon_F$, the electron is delocalized, and its contribution to the conductivity becomes metallic.

In order to be able to relate an observed negative magnetoresistance to localization of electron pairs at impurity centers or defects, it is necessary to confirm the absence of a granular structure. For all the materials to be discussed here, this has been verified by special experiments.

Negative magnetoresistance of the type of interest to us was first observed in amorphous In–O films[18] which had been carefully checked beforehand for the absence of a granular structure. These films are convenient in that it is comparatively easy to change the electron density in them and to study the temperature and magnetic field dependences of their resistance at different concentrations. Negative magnetoresistance in In–O was subsequently studied in detail.[19,20] Figure 3a is an example of field dependences of the resistance, $R(B)$, found for In–O. The field B_c at which all the curves for different temperatures intersect is referred to as the critical field. In fields $B < B_c$ the sample is in a superconducting state and a phase transition takes place at B_c. The resistance R_c at the critical field is of the same order of magnitude as the normal resistance of the film.

If the field B is slightly higher than B_c, then the sample is in the critical neighborhood of the phase transition. We shall ignore this region for the moment (returning to it later at the end of section IV). By raising the magnetic field somewhat further (in Fig. 3a, a field ($B \sim B_{\max}$) should be taken), we can determine the state of the sample by making the extrapolation $R^{-1}(T) \equiv \sigma(T) \overset{T\to 0}{\to} \sigma(0)$. In the experiment shown in Fig. 3a this extrapolation implies that the insulator region is replaced by a metallic region at a field of 10 T.

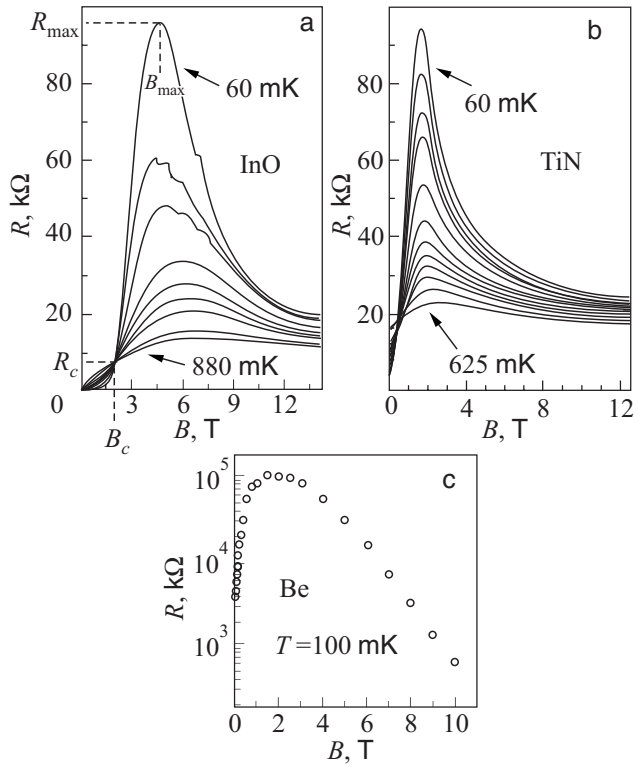

FIG. 3. Negative magnetoresistance in a transverse field in films made of different materials that are superconducting without a field: (a) In–O film of thickness 20 nm,[9] (b) Ti–N film of thickness 5 nm,[22] and (c) film of amorphous Be with a thickness just below critical, so that the resistance at the zero point is nonzero.[23]

The properties of the resulting state, as an insulator, can be characterized by the ratio $R_{\max}/R_c$ at some sufficiently low temperature. For the film of Fig. 3a, this ratio corresponds to slightly more than an order of magnitude difference at 70 mK. A state has been found[20] in which the resistance increased by more than 5 orders of magnitude compared to the critical $R_c \approx 5$ kΩ at 70 mK. The temperature dependences of the resistance have an activation character over a wide range of field, i.e.,

$$R(T) = R_0 \exp(T_0/T). \tag{22}$$

The activation energy T_0 depended on the magnetic field B and reached a maximum of about 1.7 K at $B_{\max}$. The activation energy gradually fell off when the field was increased in the region $B > B_c$.

Thus, amorphous, quasiuniform (i.e., not granular) films of In–O with an oxygen deficit were found to behave as follows:

— they become an insulator after destruction of superconductivity by a magnetic field and remained so over a wide range of fields;
— when the field was increased the temperature-induced conductivity of these films gradually decreased;
— at a sufficiently high field an insulator-metal transition takes place[19] or the sample comes very close to a metallic state;[20] and,
— the resistance in a high field returns to the level of R_c.

All of these properties fit into a picture of localized pairs, in which the electrons are localized only owing to a

superconducting interaction because their single-particle energy $\varepsilon^{(1)}$ in Eq. (21) is positive. If the initial state in the same material, amorphous In–O, is taken to be one which is not an insulator in zero field, then a negative $\varepsilon^{(1)}$ can also be observed in it: at a field of 15 T the resistance still had an activation character and varied according to a Mott law, Eq. (2) with $\nu=4$.[21]

The fact that $\partial R/\partial B<0$ over a very wide range of magnetic fields is explained by two facts. First, Δ_L decreases gradually with increasing field,

$$\Delta_L(B) = \Delta_L(0) - \tilde{g}\mu_B B \tag{23}$$

($\tilde{g}$ is the effective g-factor and μ_B is the Bohr magneton). Second, $\Delta_L(0)$ itself has a dispersion, which was mentioned above in connection with Eq. (21).

A natural question arises: how universal is this effect, i.e., is a superconducting-insulator transition in a uniform, non-disordered system always accompanied by a resistance peak and negative magnetoresistance in strong magnetic fields? As shown in Fig. 3, similar magnetoresistance behavior is observed in Ti–N films, as well as in ultrathin Be films. The two-dimensional superconducting electron system at the interface between two layered oxides $LaAlO_3$ and $SrTiO_3$, each of which is an insulator, behaves similarly to Be films: with a high carrier concentration, that two-dimensional system is a superconductor and with a low concentration, an insulator. Applying a transverse magnetic field to this interface-insulator initially causes an increase and then a drop in the magnetoresistance to values considerably lower than the original resistance at $B=0$.[24]

Nevertheless, the insulator-superconductor transition appears not to be close enough for localized pairs to appear in the insulator. A classical example, which has been studied in greatest detail, is ultrathin films of amorphous Bi, on which the technique of observing superconductor-insulator transitions was developed.[25] In ordinary ultrathin films of amorphous Bi, deposited with great care to prevent granule formation, a transition is always observed, while, if it does occur, magnetoresistance is at a level of one percent.[26–28] On the other hand, amorphous Bi provides additional material for thought. Bi films deposited by the standard method on a perforated substrate will manifest both a transition and negative resistance.[29] (See Fig. 4.) Oscillations at low fields can also be seen in Fig. 4; these are associated with so-called frustrations. We return to frustrations below, in section IV C. Here they can be regarded simply as evidence of the presence of holes in the lattice film.

Thus, we assume that the magnetoresistance peak and the negative magnetoresistance in high fields on the insulator side in the neighborhood of the superconductor-insulator is a convincing sign of pair localization (i.e., of pairwise correlations of localized carriers). Based on a single experiment[29] it is difficult to say whether it was holes in the film, or something else, that led to the localization of pairs on amorphous Bi films. However, factors do certainly exist which can enhance or suppress pairwise correlations of localized carriers in a particular material. We return to this question in section V and have more to say about experiments on a perforated substrate at the end of section IV C.

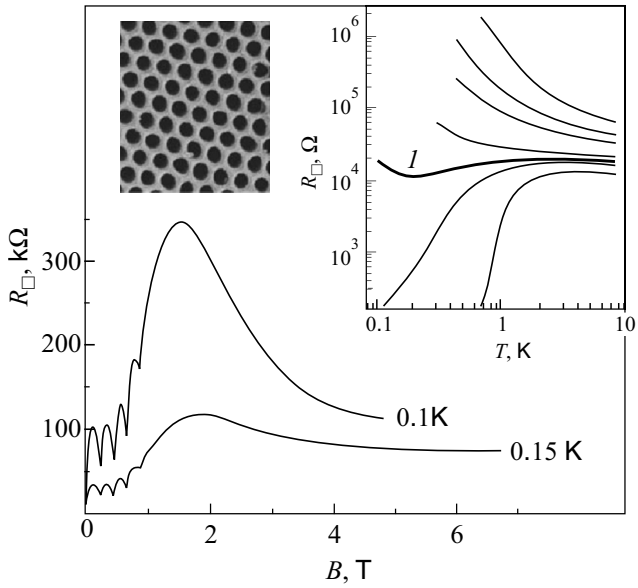

FIG. 4. (Top left) A substrate of aluminum oxide on which a Bi film was sputtered step-by-step, gradually increasing its thickness; the radius r_{hole} of the holes is about 27 nm and the distance between centers is about 100 nm. (Top right) Temperature variation in the resistance of the amorphous Bi film as its thickness b is increased (from top to bottom). The thick curve (1) is the curve for which the field dependence for two different temperatures is plotted below.[29]

B. Binding energy of electron pairs—the superconducting pseudogap

We now formulate a definition to which we shall adhere in the following. By pseudogap we mean a minimum, induced by a superconducting interaction, in the density $g(\varepsilon)$ of single-particle states on the Fermi level in a system which is not in a coherent dissipationless state. This definition includes the long and well known minimum of $g(\varepsilon)$ in the fluctuation regime of ordinary superconductors for $T>T_c$,[15] as well as the states of an ideal two-dimensional superconductor in zero magnetic field in the temperature range of Eq. (18) where Cooper pairs coexist with vortices caused by dissipation. A finite temperature interval analogous to Eq. (18) also exists when disorder is present as well as in magnetic fields.

A fundamentally new possibility for formation of a pseudogap is through the influence of localized pairs on $g(\varepsilon)$. Until recently there were no experimental measurements of $g(\varepsilon)$ and the pseudogap in it in the neighborhood of superconductor-insulator transitions. Recently, studies of this sort have been made using low-temperature scanning tunnel microscopy. Its remarkable capabilities and its problems are clearly evident in the studies of TiN films in Ref. 30.

These measurements were made on TiN films with thicknesses of 5 nm. The resistance was measured along with the current-voltage characteristic at each temperature. This made it possible to compare the evolution of the density of states $g(\varepsilon)$ with the resistive transition curve. (See Fig. 5).

This comparison shows the following: at the lowest temperatures the density of states curve looks like an ordinary plot for a superconductor, with a drop to zero in the region of $\varepsilon_F \pm \Delta$ and two coherent peaks on the sides. When dissipation appears (somewhere in the region of the BKT transition; see Fig. 2 for a comparison) the coherent peaks go to zero

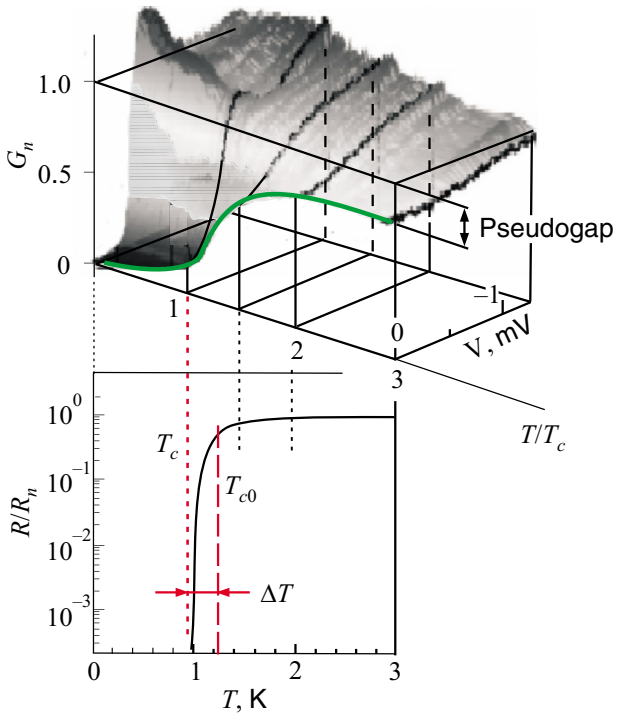

FIG. 5. Density of states near the Fermi level as a function of temperature on a TiN film (G_n is the normalized differential conductivity); the dark curves on the $G_n(T,V)$ surface are plots of $G_n(T)$ at four temperatures, $T_c \approx 1$ K, $1.5T_c$, $2T_c$, and $3T_c$.[30] As a comparison, the resistive curve for the superconducting transition is plotted below on a suitable scale (T_c is the BKT transition temperature, T_{c0} is the superconducting transition temperature, and ΔT is the temperature interval (18); cf. Fig. 2).

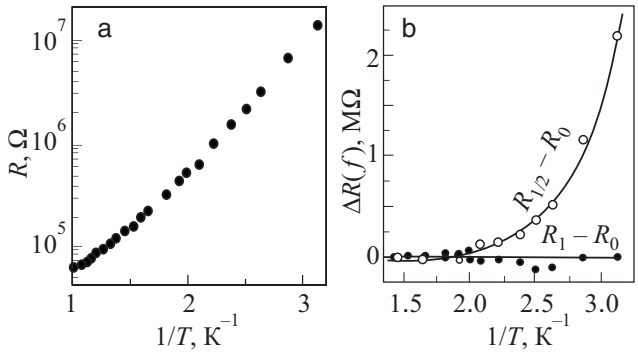

FIG. 6. Behavior of a perforated Bi film on the nonsuperconducting side of the quantum transition. A temperature dependence of the film resistance showing that the film is in an insulator state (a); temperature dependences of the additional resistance $\Delta R = R_f = R_0$ of a film with a lattice of holes at fields $f = 1/2$ and f = 1 compared to the resistance R_0 without a field.[32] (b).

and the minimum near ε_F becomes shallower. In this region the Cooper pairs move in a gas of vortices and antivortices which induce fluctuations in the phase of the order parameter. Some of the electrons from the neighborhood of the Fermi level are bound in pairs and this reduces the density of single-particle states, but there is no coherence.

Then the minimum of $g(\varepsilon)$ spreads out, although it is retained up to comparatively high temperatures. The problem is that here it is difficult to distinguish whether this minimum is evidence of pair localization, is caused by the superconducting interaction in the Cooper channel, i.e., by ordinary superconducting fluctuations, or is an Aronov-Altshuler correction to $g(\varepsilon)$ owing to the interelectron interaction in the diffusion channel, with no relation whatever to superconductivity. This correction becomes greater with increasing disorder and transforms into a Coulomb gap at the normal metal-insulator transition. It must be assumed that for a reliable identification of the effect from localized pairs tunnel spectroscopy will have to be combined with a high magnetic field.

C. The dimensions of localized pairs

Frustration oscillations on a perforated film in the insulator state are yet another experimental manifestation of localized pairs.[32] Ultrathin Bi films were deposited on a corundum substrate with holes of radius $r_{\text{hole}} = 23$ nm forming a lattice with a period of 95 nm. (See Fig. 4.) A layer of amorphous Ge with an additional 1 nm of Sb sputtered onto it was used to couple the film to the substrate. As a control, there was surrounding substrate without holes on which deposition was carried out in parallel and which was also tested after each increase in the thickness of the Bi film.

The oscillations are conveniently explained in terms of the concept of frustration--of the average number of quanta of the magnetic flux Φ_0 per unit cell of the lattice of holes:

$$f = BS/\Phi_0, \quad \Phi_0 = (2\pi\hbar)/2e, \tag{24}$$

where S is the area of a unit cell. Equation (24) makes it possible to measure the magnetic field in units of f. For integral frustration $f = 1, 2, \ldots$, the entire field is concentrated in the holes, so that there is none in the film and the inhomogeneity of the field is maintained by screening currents. According to classical electrodynamics this means that undamped currents flow around the holes, while the periodicity of the oscillations and the quantization condition (24) imply that the currents are formed by carriers with charge 2e, i.e., electron pairs.

For the results shown in Fig. 6, a state has been chosen just slightly deeper into the insulator region than the state for the magnetoresistance curves shown in Fig. 4. Figure 6a shows that the resistance in this state increases exponentially as the temperature is reduced with an activation energy of about 5 K. At the same time, frustration oscillations occur on the film in this state. They are characterized by Fig. 6b; there the curve with the hollow points shows how the amplitude of the oscillations increases as the temperature is lowered, while the curve with the solid dots indicates that the variation is not monotonic in the region of the first oscillations. Thus, Fig. 6b implies that over scale lengths comparable to the lattice of holes, $\sqrt{S}$, superconducting currents exist while, according to Fig. 6a, there are no superconducting currents or any conductivity at all on the scale of the sample.

Suppose that the lattice of holes has no effect on the quasiuniformity of the film near the superconductor-insulator transition and that immediately adjacent to the transition on the insulator side there are localized pairs with a localization length Λ_2 satisfying the condition (5). This makes is possible to interpret the experiment[32] as a measurement of a lower bound for the pair localization length Λ_2 in a given film with the particular values of the controlling parameters given in Fig. 6:

$$r_{\text{hole}} < \Lambda_2. \tag{25}$$

In accordance with this interpretation, on the higher resistance films, which lie deeper in the insulator region, there are still no frustration oscillations; they can only be observed near the transition. There is still no theoretical understanding of this "local Meissner effect" in a macroscopic insulator. In particular, it is no clear what restrictions the superconducting penetration depth may place on the possibility of observing this effect.

We now return to the positive magnetoresistance in In–O (Fig. 3a) on the left slope of the magnetoresistance peak for fields

$$B_c > B > B_{\max}. \tag{26}$$

It can be explained qualitatively in terms of a gradual reduction in the length Λ_2 on moving from the transition deeper into the insulator region. It is assumed that the conductivity for fields (26) is determined by diffusion and jumps by localized pairs. Thus, the reduction in Λ_2 with increasing field in this interval is accompanied by a reduced probability of jumps and an increase in the resistance. Here, however, there is an opposite effect of the field on Λ_2: an increase in the field leads to a reduction in the binding energy and an increase in a_{2B}, and therefore to an increase in Λ_2. The existence of two opposing effects probably leads to an expansion of the interval (26), with its right side $B_{\max}$ determined by the condition $\Lambda_2 \approx a_{2B}$ while the first factor ceases to operate.

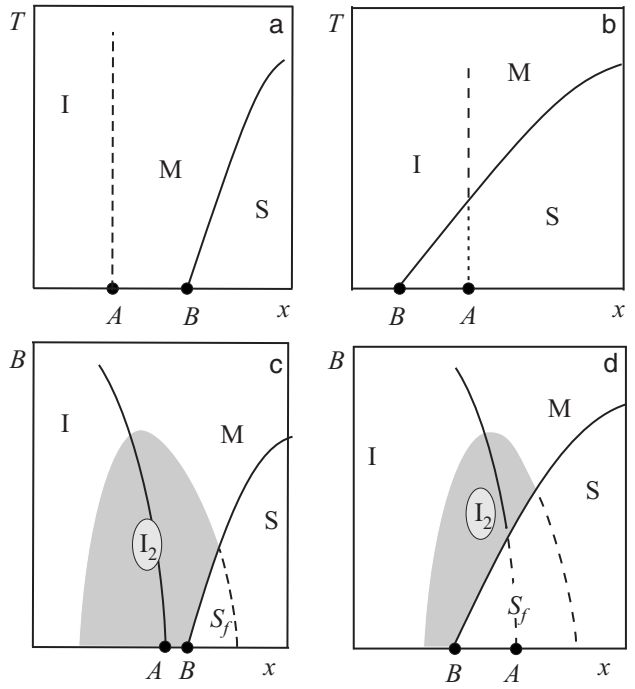

FIG. 7. (a, b) Two versions of an insulator-metal-superconductor (I-M-S) phase diagram in the (x,T) plane in zero magnetic field. (c, d) The two corresponding versions of the phase diagram in the (x,B) plane at $T=0$. The shaded region I_2 is where fractal wave functions stimulate a superconducting interaction between localized electrons. S_f denotes the assumed regions of fractal superconductivity.

V. ADDITIONAL FACTORS AIDING PAIR LOCALIZATION

In the simplest case, the electrons forming a pair can be localized in a large well of the random potential. This configuration differs from a small grain only in the absence of a high barrier along its perimeter. A significant limitation on pairing in a well of this sort is the volume occupied by a localized electron. Equation (16) sets a lower bound b_2 on the size of an isolated grain, $b > b_2$, for which the superconducting interaction influences the electron spectrum inside it. For an electron localized at a defect, the localization length Λ of the wave function plays the role of the size b. Thus, the volume occupied by a localized electron is the first important factor in the simulation of superconducting correlations between localized electrons.

The electrons of a pair are not necessarily localized on a single defect; phonon attraction is long-range. However, the average distance $s \sim (g_0\Delta)^{-1/3}$ between the electrons that we estimated in Section III B in discussing Eq. (20) may be too big. For pairing it is important that the distance between localization centers should be as small as possible. Thus, the second important factor in the stimulation of pairing is the existence of close-lying centers. Each of the localized electrons must then occupy a fairly large volume.

We now examine these two factors.

A. Closeness of the metal-insulator transition, real or virtual

In general, as the controlling parameter x is varied (say, the electron concentration is raised) a disordered insulator can become a superconductor or a normal metal. The complete phase diagram encompasses not two, but three states of the electron system: insulator (I), normal metal (M), and superconductor (S). Two versions of the phase diagram in the (x,T) plane for a three-dimensional electron system are illustrated schematically in Figs. 7a and 7b. In diagram a, as x is varied at zero temperature there are two successive transitions, $\text{I} \rightarrow \text{M} \rightarrow \text{S}$. It is known that the metal-insulator transition shows up in the (x,T) plane as an isolated point on the abscissa, so that the concept of an insulator is strictly defined only for $T=0$.[34] Thus, the vertical dashed line in Fig. 7a is somewhat arbitrary. It shows that in the strip I, extrapolating the conductivity to $T=0$ yields zero, and in the strip M, a finite value.

If, on the other hand, a single step transition $\text{I} \rightarrow \text{S}$ takes place in the system, then the virtual point $x=A$ still is in the superconducting region; if it were possible to turn off the superconducting interaction, the system would not remain an insulator with increasing x but would become a normal metal at another value of the controlling parameter. This version is shown in Fig. 7b.

In reality, the points A and B are close to one another in both cases, so that serious experimental efforts are sometimes required to determine which version applies to a given system. Since the region where localized pairs can appear is in the neighborhood of the point B, when point A is close it has a significant influence on the pairing process. This was first pointed out in Ref. 35 and the model was justified and expanded in a later paper.[36] The mechanism for this influence is the following.

Far from the metal-insulator transition the localization length Λ which shows up in the asymptote (1) is defined by the Bohr radius, $\Lambda \approx a_B$. On approaching the transition, the tails of the wave functions (1) begin to overlap and the lo-

calization length Λ increases. The way Λ increases on approaching the transition is determined by the structure of the wave functions. It is known that near the transition, on scales shorter than Λ, the wave functions have a fractal character with a fractal dimensionality $D_f < 3$. Numerical calculations[37] show that near a standard 3D Anderson transition, $D_f = 1.30 \pm 0.05$. The fractal character of the wave function also intrinsically increases its characteristic size Λ, conserving the volume within which the square of the modulus of the wave function is nonzero. Special calculations[36] showed that Cooper pairing is also realized with these kinds of fractal wave functions.

In the language of the phase diagrams a and b of Fig. 7, we can say that to the left of the point *A* there is an range of values of the controlling parameter within which the wave functions of localized normal electrons are distended owing to the fractal character, so that they are subject the effect of the superconducting interaction. The left end of this range is defined by the equation $\delta\epsilon = \hbar\omega_D$.

The electron wave functions have a fractal character on both sides of the Anderson transition. On the metal side there is also a length that diverges at the transition; usually it is usually referred to as the correlation length and denoted by ξ. With distance from the transition it decreases and transforms into the mean free path l (cf. Eqs. (3) and (5)), so that

$$l \leqslant \xi \leqslant \infty. \tag{27}$$

Differences exist only at large distances $r \gg \xi$, where besides being exponentially damped (Eq. (1)) the wave functions behave as for ordinary delocalized electrons.

Therefore, *closeness of the metal-insulator transition facilitates localized pair formation in the neighborhood of the superconductor-insulator transition.*

In Figs. 7c and 7d, the shading indicates the regions I_2 in the (x, B) plane where the fractal character of the wave functions eases the conditions for pairing of localized electrons. These regions are limited above by magnetic field-induced processes that destroy the pairs. In (c) this region is mainly to the left of the point *B* and in (d), mainly to the right. According to experiments on negative magnetoresistance, both variants of the phase diagram are realized in practice: variant (c) in Be films and $LaAlO_3/SrTiO_3$ heterostructures and variant (d) in InO and TiN (this is confirmed by other experimental data gathered in a review[4]).

The extremely interesting superconducting regions S_f are also noted in Figs. 7c and 7d. These have been referred to as fractal superconductivity regions.[35,36] Studies of fractal superconductivity are obviously something for the future.

B. "Chemical predistribution" to pair localization

It is known that correlations in a random potential can fundamentally change the localization properties of the medium. This is especially clear in the one-dimensional case. For example, if impurities are distributed in the form of pairs with a fixed distance between them, then, despite a random distribution of these pairs, the electron spectrum will include energies for which an electron is delocalized (dimer model[33]). Clearly, correlations in a random potential can play an important role in the formation of localized pairs.

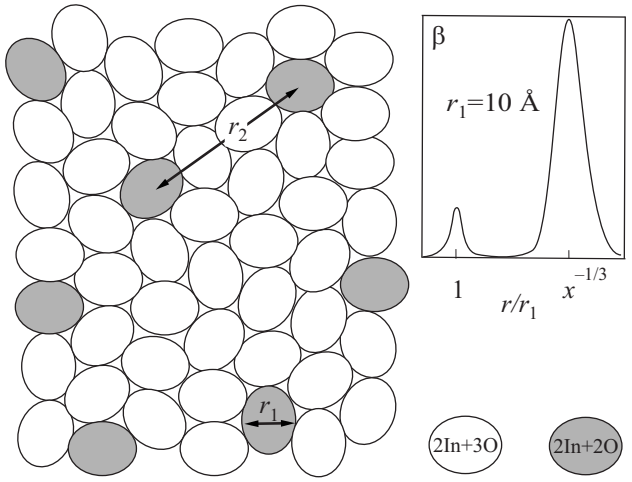

FIG. 8. Schematic illustration of the distribution of oxygen vacancies in amorphous In_2O_{3-x}. Two electrons can be localized in each of the shaded regions. The function $\beta(r)$ in the graph is the probability of finding another localized electron at a distance r from a localized electron.

Let us consider amorphous In–O as an example. The structural element of this material is a configuration of five atoms [2In+3O], within which all the valence electrons form parts of covalent bonds, as in an In_2O_3 molecule, so they are strongly bound. The chemical composition of the real amorphous material is In_2O_{3-x}. A fraction x of the structural units has an oxygen vacancy and the two valence electrons immediately adjacent to each vacancy are weakly bound to the ionic core and easily delocalized, leaving pairwise correlated wells in the random potential (see Fig. 8).

We introduce the probability $\beta = n(Q(r)+1)d^3r$ of a localized electron in a volume d^3r such that another electron is localized at the coordinate origin $r=0$. Here $Q(r)$ is the pairwise correlation function (if the positions of all the localized electrons are statistically independent, then $Q(r) \equiv 0$;) and n is the concentration of electrons which are not in covalent bonds and can be delocalized or localized. For an estimate we can assume that $n = 2xV^{-1}$, where *V* is the average volume per structural unit, roughly equal to the volume V_0 of a unit cell of crystalline In_2O_3, $V \approx V_0 \approx 10^3$ Å^3, so that $n \approx 2x \cdot 10^{21}$ cm^{-3}. The function $\beta(r)$ is illustrated schematically in the upper right corner of Fig. 8. The position of the first maximum is determined by the average size of the structural unit, $r_1 \approx 10$ Å, and that of the second, by the concentration of oxygen vacancies, $r_2 \approx r_1 x^{-1/3}$. The existence of a maximum at the comparatively low $r_1 < n^{-1/3}$ causes the "predistribution" mentioned in the title of this section.

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