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Superconductivity in a percolation structure

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The superconducting properties are investigated of a structure consisting of a random mixture of metal granules and an insulator. The dependence of the shift of T_c on the concentration of the insulator and the temperature dependences of the magnetization, fluctuation heat capacity, and the conductivity are obtained.

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Results of experiments on metal–insulator mixtures have been recently published.[1] They report observation of the dependence of the resistance on the insulator concentration at temperatures much higher than the superconducting-transition temperature T_c; this dependence agrees with the predictions of percolation theory (see the review by Stauffer[2] and the references therein). A shift of T_c near the percolation threshold was also observed in these experiments. The purpose of the present paper is to explain this shift and to predict other superconducting properties of such a structure. We assume that the structure of interest to us consists of minute granules of metal randomly interconnected with one another and imbedded in an insulator.

The properties of such a structure far from the superconducting-transition point are described by percolation theory. This theory shows that the resistance vanishes at a finite insulator concentration $1-p_c$. This phenomenon is similar to a second-order phase transition. Near p_c the dependences of the resistance, of the thickness P_0 of the infinite cluster (the cluster is defined as the connected region of the conductor) and of the percolation length L (a quantity equivalent to the correlation radius in the theory of phase transitions) on p are of the form

$$\sigma\sim(p-p_c)^t,\ P_0\sim(p-p_c)^\beta,\ L\sim(p-p_c)^{-\nu}. \tag{3}$$

The exponents t, β, and ν are analogous to the critical exponents of the theory of phase transitions; they do not depend on the concrete microscopic structure. The values of the exponents are known[2]: they can be obtained, in particular, by numerical calculations. In a three-dimensional system we have $t=1.7$, $\beta=0.4$, and $\nu=0.9$. In a two-dimensional system $t=1.3, \beta=0.14$, and $\nu=1.35$. The diffusion coefficient is proportional to the conductivity:

$$D=2\varepsilon_F\sigma/dne^2.$$

It corresponds to the same exponent t as σ.

Let the characteristic microscopic dimension of the granule be much smaller than $\xi(T)$. Here $\xi(T)$ is the average correlation radius of the superconducting order parameter and is defined for clusters with dimensions much larger than $\xi(T)$. This assumption allows us regard the order parameter as constant over the granule dimension. In this case the superconducting properties of the system are determined by percolation theory. The essential assumptions needed for this purpose are: neglect of the Coulomb interaction of the electrons[3] and of the Josephson tunneling of the electrons through the insulator. The unusual superconducting properties are due to the small diffusion coefficient at large distances, which leads to a considerable broadening of the region of the order-parameter fluctuation and to a shift of T_c, as well as to the dependence of D on the distance at $r<L$, from which follow the unusual dependences of the magnetization at $\xi<L$ and of the fluctuation conductivity and of the heat capacity.

2. We write down the Ginzburg-Landau Hamiltonian for an individual cluster. In this case the influence of the proximity to the percolation point influences the low density of the cluster and the small nonlocal diffusion coefficient:

$$H=\frac{1}{2}\int d\mathbf{x}_1\,d\mathbf{x}_2\,\gamma' D(\mathbf{x}_1,\mathbf{x}_2)\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)(\nabla\psi(\mathbf{x}_1))(\nabla\psi(\mathbf{x}_2))+$$
$$+\int d\mathbf{x}\left[\alpha\tau|\psi(\mathbf{x})|^2+\frac{1}{2}\delta|\psi(\mathbf{x})|^4\right]\rho(\mathbf{x}), \tag{2}$$

where $\rho(x)$ is the density of the cluster at the point $\mathbf{x}$, and α, δ, and γ' are expressed in terms of the microscopic quantities as usual:

$$\alpha=N(0);\quad \gamma'=\frac{\pi}{4}\frac{N(0)}{T};\quad \delta=\frac{7\zeta(3)}{16\pi^2}\frac{N(0)}{T^2},\quad \tau=\frac{T-T_c}{T_c}.$$

We calculate now the shift of T_c. To this end, we consider the unperturbed Green's function $G_0(\mathbf{x}_1, \mathbf{x}_2)$ of the Hamiltonian.[1] We introduce the Fourier transform $G_0(q, \mathbf{x}, \tau)$ of $G_0(\mathbf{x}_1, \mathbf{x}_2)$ with respect to $\mathbf{x}_1-\mathbf{x}_2$:

$$G_0(\mathbf{q},\mathbf{x},\tau)=\int d\mathbf{r}\, e^{-i\mathbf{q}\mathbf{r}}G_0(\mathbf{x}+\mathbf{r},\mathbf{x}-\mathbf{r}),$$
$$G_0^{-1}=-\gamma'\frac{d}{dx_i}\rho(\mathbf{x})D(\mathbf{x},\mathbf{x}')\rho(\mathbf{x}')\frac{d}{dx_i'}+2\alpha\tau\rho(\mathbf{x}) \tag{3}$$

[(3) is the operator equation that defines G_0].

It is natural to take T_c in such a system to mean the superconducting-transition point of an infinite cluster, since it is precisely this point which is determined from the conductivity measurements. The shift of T_c (compared with a region far from the percolation threshold) is due to the increase of the fluctuation of ψ.

We estimate $\delta\tau_c$ in the three-dimensional problem in first-order perturbation theory in the term $|\psi|^4$:

$$\delta\tau_c=T\frac{\delta}{\alpha}\int\langle G(\mathbf{q},\mathbf{x},0)\rangle d\mathbf{q}, \tag{4}$$

where $\langle\ldots\rangle$ denotes averaging over $\mathbf{x}$, and G is taken for an infinite cluster. $G(q, \mathbf{x}, 0)$ can be determined from similarity considerations in percolation theory. At small q ($qL\ll 1$) the fluctuations of D and ρ are small, therefore $\rho(\mathbf{x})D(\mathbf{x},\mathbf{x}')\rho(\mathbf{x}')$ can be replaced by the function $\mathbf{x}-\mathbf{x}'$. This is the same quantity that enters in the macroscopic definition of the diffusion coefficient, therefore at $qL\ll 1$ we have

$$\langle G_0\rangle=(\gamma' D_0 q^2)^{-1}.$$

We write down G_0 for all q in the form ($\tau=0$)

$$\langle G_0\rangle=(\gamma' D_0 q^2 f(qL))^{-1},\ f(0)=1, \tag{5}$$

where $f(qL)$ is a dimensionless function. If $qL\gg 1$, then $\langle G_0\rangle$ should not depend on $p-p_c$, hence

$$f(qL)\sim(qL)^{t/\nu},\ t/\nu\approx 2,$$

therefore the integral in (4) can be estimated:

$$\delta\tau_c\approx T\frac{\delta}{\alpha\gamma' D_0 L}\approx A(p-p_c)^{-(t-\nu)},\quad A\approx T_c\frac{\delta}{\alpha\gamma' D' L'}. \tag{6}$$

Here L' is the dimension of the granule and D' is the coefficient of diffusion in it. This formula is valid also for large $\delta\tau_c\sim 1$. In this case it can be inverted and we obtain

$$T_c'=T_c A^{-1}(p-p_c)^{t-\nu}.$$

To estimate $\langle\xi(T)\rangle$ it is necessary to compare the second term of (3) with the first. At $qL\ll 1$ the second term fluctuates little and coincides with $\alpha\tau P$; at $qL\gg 1$, from similarity considerations, it is proportional to $q^{\beta/\nu}$. Therefore at $\xi<L$ (this the only case of interest to us from now on)

$$\gamma'\xi^{-2}D_0(L/\xi)^{t/\nu}\approx\alpha\tau(L/\xi)^{\beta/\nu}P_0,$$
$$\xi\approx(B\tau)^{-\nu/(2\nu+t-\beta)},\ B\approx\alpha/\gamma' D'(L')^{(t-\beta)/\nu}. \tag{7}$$

We can now estimate $\langle G_0\rangle$ also at $\tau\neq 0$. If $q\xi\gg 1$, then $\langle G_0(q,\tau)\rangle=\langle G_0(q)\rangle$ and is given by formulas (5) and (6). At $q\xi\ll 1$ we can retain in (3) only the second term and

$$\langle G_0(q,\tau)\rangle=\langle 1/\alpha\tau\rho(x)\rangle_q,$$

where $\langle\ldots\rangle_q$ means that the averaging over x must be carried out over distances $\sim q^{-1}$; from similarity considerations

$$G_0(q,\tau)=\frac{1}{\alpha\tau P(qL)}. \tag{8}$$

Here $P(qL)$ is the density of a cluster of size q^{-1}.

The fluctuation correction to the heat capacity is determined in terms of a four-particle Green's function, whose value in the zeroth approximation is

$$\delta c=-T\frac{d^2F}{dT^2}=-\frac{\alpha^2}{T^3}\left\langle\int\rho(\mathbf{x}_1)G_0^2(\mathbf{x}_1,\mathbf{x}_2)\rho(\mathbf{x}_2)d\mathbf{x}_2\right\rangle_{\mathbf{x}_1}.$$

We consider the Fourier transform of

$$g=\rho(\mathbf{x}_1)G_0(\mathbf{x}_1,\mathbf{x}_2)\rho(\mathbf{x}_2)$$

with respect to $\mathbf{x}_1-\mathbf{x}_2$. We obtain the quantity $\langle gq(\mathbf{x},\tau)\rangle_x$ in analogy with $\langle G_0\rangle$:

$$g_q\sim(p-p_c)^{-t+2\beta}q^{-2}\ (qL\ll 1);$$
$$g_q\sim q^{-(t-2\beta)/\nu-2}\ (qL\gg 1,\ q\xi\gg 1)$$
$$g_q\sim q^{\beta/\nu}\ (q\xi\ll 1).$$

We rewrite the fluctuation correction in the form

$$\delta c_{cl}=-\frac{\alpha^2}{T^3}\left\langle\int G_0(\mathbf{q},\mathbf{x})g_q(x)d\mathbf{q}\right\rangle_x. \tag{9}$$

For an estimate we can represent the mean value in (9) by a product of four mean values and obtain

$$\delta c_{cl}\sim\xi^{(2t-2\beta)/\nu+1}\sim\tau^{-(2t-2\beta+\nu)/(2\nu+t-\beta)},$$
$$\delta c_{cl}\sim\tau^{-(2t-2\beta+2\nu)/(2\nu+t-\beta)} \tag{10}$$

for three- and two-dimensional problems, respectively.

Formula (10) determines the contribution made to the heat capacity by one cluster of size larger than ξ. The total fluctuation heat capacity is obtained by multiplying this contribution by the fraction of matter belonging to clusters with dimensions larger than ξ, i.e., $P(\xi)\sim\xi^{-\beta/\nu}$. This formula follows from similarity considerations and $P(L)=P_0\sim(p-p_0)^\beta$. The final answer for the fluctuation correction to the heat capacity is

$$\delta c\sim\tau^{-(\nu+2t-3\beta)/(2\nu+t-\beta)}\approx\tau^{-1}\ (3D),$$
$$\delta c\sim\tau^{-(2t-3\beta+2\nu)/(2\nu+t-\beta)}\approx\tau^{-1,3}\ (2D). \tag{11}$$

The condition that allows us to use in the derivation of (11) the zeroth approximation is the smallness of the fluctuations. Let T_c and T_c' be respectively the transition temperatures without and with allowance for the fluctuations. Then at $T_c'<T<T_c$ the fluctuations are certainly large. We estimate the temperature above which one can regard the fluctuations as small. To this end, we compare the fluctuations of the order parameter in the volume ξ^d with its equilibrium value:

$$\frac{\alpha}{\delta}\tau\gg\left(\frac{\xi^d\alpha\tau P(\xi)}{T}\right)^{-1/2}.$$

We obtain

$$\tau\gg\left[T\frac{\delta^2}{\alpha^3}(L')^{-\beta/\nu}B^{-(3\nu-\beta)/\nu}\right]^{(2\nu+t-\beta)/(3\nu+3t-2\beta)}.$$

3. The fluctuation correction to the conductivity, in the lowest order in the fluctuations, is determined by a sum of Maki-Thomson[4] and Aslamazov-Larkin[5] diagrams. We calculate the latter (which is of importance in a three-dimensional system). It is more convenient to calculate it by using the time-dependent Ginzburg-Landau equations, in which it is given by diagram a of Fig. 1, and is equal to

$$\delta\sigma=\left\langle \frac{1}{3}\pi e^2\int\rho(\mathbf{x})D(\mathbf{x},\mathbf{x}_1)\rho(\mathbf{x}_1)\frac{d}{d\mathbf{x}_1}\rho(\mathbf{x}_2)D(\mathbf{x}_2,\mathbf{x}_3)\times\rho(\mathbf{x}_3)\frac{d}{d\mathbf{x}_2}\frac{\partial}{\partial\tau}G_0^2(\mathbf{x}_1,\mathbf{x}_2)\,d\mathbf{x}_1\,d\mathbf{x}\,d\mathbf{x}_3\right\rangle_{x_2}. \tag{12}$$

By way of estimate we note that $\partial G_0^2(\mathbf{x}_1,\mathbf{x}_2)/\partial\tau$ decreases rapidly at $x_1-x_2>\xi$, therefore the characteristic distances in the integral (12) are of the order of ξ. We replace all the quantities in (12) by their values averaged over these distances. We obtain

$$\delta\sigma\approx e^2/\tau\xi\sim\tau^{-(\nu+t-\beta)/(2\nu+t-\beta)}\approx\tau^{0.7}. \tag{13}$$

The Maki-Thomson diagram makes in a three-dimensional system a contribution of the same order of magnitude, but with different coefficients.

In a two-dimensional system, the main contribution is made by the Maki-Thomson diagram (b of Fig. 1), which is the determined by the distance region $|\mathbf{x}_2-\mathbf{x}_3|\sim\xi$. The four-pole $K(\mathbf{x},\mathbf{x}_2,\mathbf{x}_3,\mathbf{x}_1)$ in diagram b can be estimated. At distances exceeding L, the value of K depends only on the coordinate difference and

$$\int K\,d\omega\,d\mathbf{x}_1\,d\mathbf{x}_2\,d\mathbf{x}_3\,e^{i\mathbf{q}(\mathbf{x}_2-\mathbf{x}_3)}=\int\frac{D\,d\omega}{(Dq^2+i|\omega|)^2}=\frac{1}{q^2}$$

does not depend on $p-p_c$. Consequently, at distances less than L, the dependence of K on the distance does not have an additional exponent, so that the fluctuation correction is

$$\delta\sigma\approx\frac{e^2}{d}\int\frac{dq}{q}\frac{1}{\tau}\approx\frac{e^2}{d\tau}\ln\frac{\tau}{\tau_0}. \tag{14}$$

Here τ_0 is a cutoff at small momenta on account of the energy relaxation or of the fluctuations of ψ.[6] The latter quantity is also anomalously large and is determined in a homogeneous system by the formula

$$\tau_0=\frac{8T^2}{\pi}\int d\mathbf{q}\frac{\partial}{\partial\tau}G_0(\mathbf{q}).$$

The significant values of q in this formula are $\sim\xi^{-1}$, therefore

$$\tau_0\sim(20\tau N(0)dD(\xi))^{-1}.$$

4. To determine the magnetic properties of the system we consider first the behavior of clusters with small dimensions $l<\xi(\tau)$ in a magnetic field. In such clusters, the modulus of the order parameter is constant. To estimate the free energy of a small cluster in a magnetic field it is important to ascertain what fraction of its volume belongs to rings of a given size. We shall denote it by dR_l/dl; R_l is the volume fraction belonging to rings with radii larger than l. In similarity theory, $R_l\sim l^{-\beta'/\nu}$ $(l<L)$. We now obtain upper and lower-bound estimates of β'. It must be larger than the "transport" β^t introduced by Kirkpatrick[7], which describes the density of the nodes belonging to the "core" of the cluster. The core is defined as the aggregate (according to Ref. 7) of the nodes that can be interconnected by at least two paths. Nodes that do not belong to the core certainly do not contribute to the conductivity and do not belong to rings $\sim L$. Numerically, $\beta^t=0.5$ to 0.6 in a two-dimensional system and $\beta^t=0.9\pm0.1$ in a three-dimensional one.

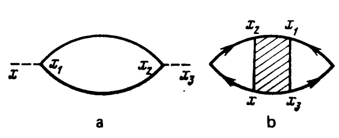

FIG. 1.

On the other hand, the conductivity of an infinite cluster cannot exceed the conductivity due to the matter contained in the rings of size L in an infinite cluster. The density of matter is $(p-p_0)^{\beta+\beta'}$, consequently $t-\beta>\beta'>\beta^t$. Numerically $1.0>\beta'>0.6$ in a two-dimensional system and $1.3>\beta'>0.9$ in a three-dimensional one.

If the flux of the magnetic field through the superconducting ring is less than the flux quantum, then in the estimate of the energy of this ring the phase can be regarded as constant, and A can be replaced by HR. We express the density of the free energy in the cluster in the form of an integral over the dimensions of its constituent rings:

$$F_{cl}=\left[\frac{1}{2}\gamma'\int_0^{l_{cl}}dl\frac{dR}{dl}[\rho D\rho](l)(Hl)^2-\alpha\tau P\right]\psi^2+\frac{1}{2}\beta\psi^4. \tag{15}$$

The integrand is proportional to $l^{-(t-\beta+\beta')/\nu+2-1}$. In a two-dimensional percolation structure this exponent is larger than -1, and the integral is determined by the upper limit:

$$F_{cl}\approx\frac{1}{\beta}[P\alpha\tau-R(l)\rho D\rho(Hl)^2\gamma']^2,\qquad P(l)\alpha\tau>R(l)\rho D\rho(Hl)^2\gamma'. \tag{16}$$

The condition (16) determines the maximum size of the cluster that is superconducting in the given magnetic field. The field is assumed here to be strong enough, so that this size is less than ξ and the flux H through the cluster is less than the quantum flux. The magnetization of the entire sample is

$$M=-\frac{dF}{dH}=-\frac{d}{dH}\int_0^{l_m}dl\frac{dP}{dl}\frac{1}{\beta}[\alpha\tau-R(l)\rho D(l)(Hl)^2\gamma']^2,\qquad M\sim H^{2\beta/(2\nu+\beta-\beta'-t)-1}\tau^{-\beta/(2\nu-t+\beta-\beta')}\sim H^{-0.5}\tau^{-0.25}. \tag{17}$$

With decreasing field, l_m increases until Hl_m^2 becomes equal to 1 or $l_m\sim\xi$. In weaker fields the free energy of the cluster per unit volume ceases to depend on the cluster size, since rings of size $l>H^{-1/2}$ do not contribute to the integral (15). This means that a superconducting transition of an infinite cluster will take place in such magnetic fields, i.e., this field equals to H_{c2}. We estimate now the field in which $Hl_m^2\sim1$, and then show that this field is indeed H_{c2}, i.e., $l_m<\xi$:

$$H_{c2}\approx[\alpha(\gamma'D')^{-1}(L')^{(t+\beta-\beta')/\nu}\tau]^{2\nu/(2\nu+t-\beta+\beta')}\sim\tau^{0.6}.$$

l_m is then determined by the expression

$$P(l_m)\alpha\tau \approx R(l_m)\rho D\rho(l_m)(H_{c2}l_m)^2\gamma'.$$

We divide this equation by the equation for ξ:

$$P(\xi)\alpha\tau \approx \rho D\rho(\xi)\xi^{-2}\gamma'.$$

We obtain

$$(l_m/\xi)^{(t-\beta+2\nu)/\nu} = R(l_m) \ll 1.$$

In the three-dimensional case the integral in (15) is determined by its lower limit and the properties of such a system are equivalent to a system of small ($\sim L'$) unconnected spheres whose magnetization in such magnetic fields is proportional to H.

5. When comparing the model with experiment, we must verify that Josephson tunneling through the insulator, which might also increase the role of the fluctuations, is of no importance in a real system. The effect of the tunneling can be described for the case of minute granules (of size much less than ξ, i.e., ψ is constant in each granule) by adding to the Hamiltonian (2) the term

$$\frac{1}{2}\gamma'' \int (\nabla\psi)^2 dr. \tag{18}$$

The value of (18) should be small compared with the first term in (2). This is equivalent to a resistance (at high temperatures) due to the contacts between granules much lower than the resistance due to tunneling through the insulator. This yields for the wall thickness the estimate $L' \gg a[-\ln(p-p_c)]$. It is possible that a more convenient experimental criterion is that the sample resistance at high temperatures satisfy the relations of percolation theory.

The system experimentally investigated in Ref. 1 was Hg–Xe. The resistance above the superconducting transition point was described by an exponent that coincided with the prediction of percolation theory for a three-dimensional system. In addition, the authors observed a decrease of T_c with approach to the percolation threshold. The dependence of T_c on $p-p_c$ agrees qualitatively with Eq. (6) (exponent $t-\nu=0.8$). From the data of Ref. 1 we can also estimate $A \approx 5\times10^{-3}$, which is in reasonable agreement with formula (6), the latter being more convenient for estimates when recast in the form

$$A \approx 1/(p_F l)(p_F L').$$

Here p_F is the Fermi momentum and l is the mean free path in the granule.

Unfortunately, the accuracy of the published experimental data is insufficient for a good quantitative comparison. It would be of interest to measure the fluctuation conductivity and the heat capacity of the same sample and compare them with (11) and (13). For such measurements, a stronger restriction on $p-p_c$ is needed than the condition $p-p_c \ll 1$ which is sufficient for the applicability of (6). It is necessary to have $\xi \ll L$, i.e., $L'(p-p_c)^{-\nu} \gg \xi(\tau)$, or, expressed in terms of experimentally measurable quantities:

$$(p-p_c)^{\nu-\beta/2} \ll L'(T\tau/D_0)^{1/2}.$$

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