Superdiamagnetism in a model with spontaneous currents

B. A. Volkov, V. L. Ginzburg, and Yu. V. Kopaev

P. N. Lebedev Physics Institute, USSR Academy of Sciences
(Submitted 9 January 1978)
Pis'ma Zh. Eksp. Teor. Fiz. **27**, No. 4, 221–226 (20 February 1978)

The possible nature of superdiamagnetism is discussed. Principal attention is paid to the spontaneous-current model, which can lead to the superdiamagnetic state.

PACS numbers: 75.20.Ck

1. The transition observed[1] in CuCl at a temperature $T_c \sim 150$ K into a state close to ideally diamagnetic (magnetic susceptibility $\chi \to -1/4\pi$) might seemingly be most naturally connected with high-temperature superconductivity. Inasmuch as an excitonic dielectric state[2] is apparently realized in CuCl, one can hope to realize a variant in which the superconducting transition temperature T_c in an alloyed substance is greatly increased as a result of the increase in the density of the electronic states (see[3] and Ch. 5 of[4]). In this case, however, as in ordinary superconductors ideal conductivity should be observed in addition to ideal diamagnetism (or, more

accurately, the Meissner effect). In,[1] however, the substance remains weakly conducting. In addition, peculiar strong oscillations of the magnetic moment are observed, as well as hysteresis. These singularities are still logically compatible with ordinary superconductivity, inasmuch as the samples used in[1] were polycrystalline. Therefore the individual grains (crystallites) can turn out to be insulated from one another. Hysteresis and oscillations of the moment are likewise not excluded.

2. Nonetheless, these singularities, as well as general considerations, prompt us to raise the question of the existence of superdiamagnets (susceptibility $\chi \to -1/4\pi$) that differ from ordinary superconductors. This possibility was mentioned already long ago.[5] Moreover, recently[6] a microscopic model has been pointed out, for which such a possibility is not only realistic, but pertains precisely to substances of the superconducting type. Namely, it is shown in[6] that electron-hole pairing in the two-band model with band extrema that coincide in momentum space, leads, at an imaginary order parameter and for allowed interband dipole transitions, to a state with a spontaneous current.[1)] This means, that in the ground state a local-homogeneous current with density $\mathbf{j}_0$ flows in the substance. Of course, in the stationary regime, when there is no accumulation of charges, we have div $\mathbf{j}_0 = 0$ and in the absence of an external magnetic field the total magnetic moment of the sample should be equal to zero or be quite small (we assume that the sample has gone over into the state in question by cooling without an external field), since some system of closed current domains, tubes, or filaments has been produced. The character (configuration or dimensions) of such a system at equilibrium should be determined from the condition that the free energy be minimal, in analogy with the situation for other domain structures in a great variety of substances (ferromagnets, antiferromagnets, ferroelectrics, superconductors).[10] Far from the point of the second-order phase transition (or of the first-order transition close to second order), the order parameter (in our case, the spontaneous current $\mathbf{j}_0$) can usually be regarded as specified ($\mathbf{j}_0 = \text{const}$). Near the transition point, to the contrary, the order parameter is itself determined from the condition that the free energy be a minimum, and this can lead to a radical change in the character of the domain structure and the type of the domain walls.[11] In this connection, even in the model with spontaneous currents, depending on the values of the parameters, one can conceive of a great variety of situations corresponding to orbital ferromagnetism, orbital antiferromagnetism, or superdiamagnetism.

3. Assume that the produced structure of the currents at the considered temperature T is rigid enough in the sense that in a weak magnetic field it remains practically unchanged and, specifically, the current filaments cannot rotate with the field. Such a system of closed filaments is qualitatively equivalent to an assembly of fixed annular macromolecules carrying a certain orbital current, i.e., having a magnetic moment. The action of a sufficiently weak external magnetic field under such conditions is qualitatively described by the Larmor theorem, i.e., it reduces to precession of the electrons with angular velocity $\vec{\Omega} = (e/2mc)\mathbf{B}$ ($-e$ and m are respectively the charge and mass of the electron). The induced magnetic moment of the filament is

$$\vec{\mu} = -\frac{e}{2c}\Sigma[\mathbf{R}\times\mathbf{v}] = -\frac{e^2}{4mc}\Sigma[\mathbf{R}\times[\mathbf{B}\times\mathbf{R}]] = -\zeta\frac{e^2 n_1}{mc^2}\overline{R^2}\mathbf{B},$$

where $\overline{R}^2$ is the mean squared dimension (radius) of the filamentary ring, n_1 is the number of electrons in the ring, and $\zeta \sim 0.1$ (for a spherically symmetrical distribution of the charges we have $\zeta = 1/6$, and the well known formula for the moment of a diamagnetic atom is obtained; a quantum-mechanical calculation yields the same result). The magnetization per unit volume is therefore

$$M = -\zeta \frac{e^2 n_1 n_2}{mc^2} \overline{R^2} B = \chi' B = \frac{\chi}{1 + 4\pi\chi} H$$

(n_2 is the number of filaments per unit volume, $\zeta' \sim \zeta$, and $\chi = M/H$ is the usually introduced magnetic susceptibility). Obviously $n_1 n_2 \sim n$ is the concentration of the electrons that go over into the state with spontaneous current. Assuming by way of example $n \sim 10^{19}$ cm^{-3}, we get $|\chi'| \sim 10^{-13} n R^2 \gg 1$ at $(R^2)^{1/2} \gg 10^{-3}$ cm. Of course, at $|\chi'| \gtrsim 1$ the external field in the sample cannot be regarded as homogeneous, and if formally $|\chi'| \gtrsim 1$, then we have in the sample $B \to 0$ and $\chi = \chi'/(1 - 4\pi\chi') \to -1/4\pi$. The foregoing arguments, although elementary, offer in our opinion convincing evidence that the model considered has diamagnetic properties under the indicated conditions.

4. For a quantitative description of the system with spontaneous currents it is natural to start with a thermodynamic potential of the type (see[7,10,11]):

$$\Phi = \int dV \left\{ \frac{H^2}{8\pi} + f(j^2) + \frac{\delta (\mathrm{rot}\, \mathbf{j})^2}{2} \right\}, \tag{1}$$

$$\mathrm{rot}\, \mathbf{H} = \frac{4\pi}{c} \mathbf{j}, \qquad \mathrm{div}\, \mathbf{H} = 0.$$

where we can put near T_c

$$f(j^2) = \frac{\Lambda}{2} j^2 + \frac{b}{4} j^4, \quad \Lambda = a^2 (T - T_c), \qquad b > 0; \tag{2}$$

where j is the current density and should be determined from the condition that Φ is minimal [anisotropy is neglected in Eqs. (1) and (2)]. Neglecting the magnetic energy, the square of the density of the spontaneous current is determined by the condition $\partial f(j^2)/\partial j^2 = 0$, whence we get in the case of (2) $j_0^2 = -\Lambda/b = a^2(T_c - T)/b$. In the real problem, minimization of the functional (1) leads to a domain structure. If, as applied to a single domain, we neglect the surface-energy density $\delta(\mathrm{curl}\, \mathbf{j})^2/2$, then (at $j' \ll j_0$):

$$\Phi = \int dV \left\{ \frac{H^2}{8\pi} + f(j_0^2) + 2 j_0^2 \left[\frac{\partial^2 f}{(\partial j^2)^2} \right]_0 (j')^2 \right\}, \quad \mathbf{j}' = \frac{c}{4\pi} \mathrm{rot}\, \mathbf{H} - \mathbf{j}_0 .$$

Minimization of this functional leads to the London equation

$$\mathrm{rot}\, \Lambda' \mathbf{j}' = -\frac{1}{c} \mathbf{H}, \quad \Lambda' = 4 j_0^2 \left[\frac{\partial^2 f}{(\partial j^2)^2} \right]_0 \qquad \text{and} \quad \Delta \mathbf{H} - \frac{4\pi}{\Lambda' c^2} \mathbf{H} = 0;$$

i.e., to diamagnetic screening of the field (the depth of penetration is $\lambda = \sqrt{\Lambda' c^2/4\pi}$ as estimated from the formula

$$\lambda = \frac{\sqrt{mc^2}}{4\pi e^2 n} \sim 2\times 10^{-4}\ \text{cm}$$

at $n \sim 10^{19}$).

Screening is obtained also from a more consistent solution of the problem on the basis of expressions (1) and (2). For current filaments of radius r, having a surface tension α per unit surface (so that the surface energy per unit length of filament is $2\pi\alpha r$), we obtain from the condition that the sum of the magnetic and surface energies be minimal (the density j_0 is assumed specified, corresponding to the region far from T_c) the estimate[5]

$$r \sim \left(\frac{\alpha c^2}{j_0^2}\right)^{1/3}. \tag{3}$$

It is important that r does not depend on the dimensions of the sample. This result agrees with the one obtained already by Landau[7] on the basis of an equation of the type (1), according to which $\alpha \sim \delta j_0^2/r$. If we put $R \sim r \sim 10^{-3}$ cm, then $\alpha/j_0^2 \sim 10^{-30}$ (see (3) and, say at $\alpha \sim 1$ erg/cm^2, the density of the spontaneous current is $j_0 \sim 10^{15}$ cgs units $\sim 3\times 10^5$ A/cm^2, corresponding to a field $H = 2\pi r j_0/c \sim 100$ Oe at the filament boundary. All these figures indicate, of course, only that the obtained values are possible (or, if you wish, not contradictory).

5. If a transition to the state with spontaneous currents in question actually takes place in CuCl, then the appearance of superdiamagnetism, of oscillations of the moment, and of hysteresis can be qualitatively easily understood. The absence of high conductivity (or of superconductivity) is less clear, but at any rate does not contradict the model. In fact, the system of the filaments with current is assumed to be fixed and need not necessarily "short out" an external electric circuit under the influence of a weak external electric field. Moreover, in the model of[6] in the linear approximation, a homogeneous electric field does not change the current, i.e., the usual electric conductivity at $T=0$ is equal to zero (this very possibility was already mentioned in[5]). It is natural to assume, however, that under definite conditions the spontaneous current can go over, on the boundary with the normal metal, into a normal current, and a superconductivity of sorts can thus be observed. The most direct way of verifying this hypothesis is by magnetic measurements. Thus, in a sample with spontaneous currents, in the absence of an external field, there should be present local magnetic fields both in the interior of the sample and near its surface. It is apparently even simpler to verify the hypothesis that when the sample is cooled from the region $T > T_c$ in an external magnetic field it acquires a paramagnetic moment. Turning on a field at $T \ll T_c$ can, depending on the interplay between the different parameters, either leave the sample in the ferromagnetic state (we have in mind the presence of a constant magnetic moment; see, incidentally,[12]), or lead to a state without a moment. In a region close enough to T_c, the external field for a second-order transition should greatly alter the magnetic structure, etc..

We are, of course, well aware that the observations reported in[1] call for confirmation, and their explanation within the framework of a model with spontaneous currents is at present only a hypothesis that calls for experimental verification and further theoretical analysis.

[1)]A state with spontaneous current is preferable to an excitonic dielectric when account is taken of scattering by impurities and defects.[6] The fact that superdiamagnetism is observed only after deep cooling and vanishes with time[1] can be attributed in fact to a change in the number of defects. It should be noted that the hypothetical existence of spontaneous current was discussed in its time[7-9] with an aim at explaining superconductivity. This approach, however, had encountered great difficulties[5] as applied to "ordinary" superconductors and was not fruitful. The state with spontaneous currents, considered in[6], differs in fact substantially from the usual superconducting state. At the same time it must be emphasized that the Landau model[7] has in fact a direct bearing on the possible existence, discussed by us, of a "superdiamagnetic" state.

[1]N. B. Brandt, S. V. Kuvshinnikov, A. P. Rusakov, and M. V. Semenov, Pis'ma Zh. Eksp. Teor. Phys. **27**, 37 (1978) [JETP Lett. **27**, 33 (1978)].

[2]A. P. Rusakov, S. G. Grigoryan, A. V. Omel'chenko, and A. E. Kadyshevich, Zh. Eksp. Teor. Fiz. **72**, 726 (1977) [Sov. Phys. JETP **45**, 380 (1977)].

[3]Yu. V. Kopaev, Zh. Eksp. Teor. Fiz. **58**, 1012 (1970) [Sov. Phys. JETP **31**, 544 (1970)]; see Nekotorye voprosky sverkh-provodimosti (Some Problems of Superconductivity), Nauka, 1975, p. 3.

[4]Problema vysokotemperaturnoĭ sverkhprovodimosti (The Problem of High-Temperature Superconductivity), ed. by V. L. Ginzburg and D. A. Kirzhnits, Nauka, 1977.

[5]V. L. Ginzburg, Usp. Fiz. Nauk **48**, 25 (1952); Fortschr. d. Phys. **1**, 101 (1953).

[6]B. A. Volkov and Yu. V. Kopaev, Pis'ma Zh. Eksp. Teor. Fiz. **27**, 10 (1978) [JETP Lett. **27**, 7 (1978)].

[7]L. Landau, Phys. Z. Sowjetunion **4**, 43 (1933).

[8]W. Heisenberg, Z. Naturforsch. Tel. A **2**, 185 (1947); Ann. Phys. (Leipzig) **3**, 289 (1948).

[9]H. Koppe, Ergebnisse d. exakten Naturwissensch. **23**, 283 (1950).

[10]A. Hubert, Theory of Domain Walls in Ordered Media (Russ. transl.), Mir, 1977.

[11]L. N. Bulaevskiĭ and V. L. Ginzburg, Zh. Eksp. Teor. Fiz. **45**, 772 (1963) [Sov. Phys. JETP **18**, 530 (1964)].

[12]V. L. Ginzburg, Zh. Eksp. Teor. Fiz. **31**, 202 (1957) [Sov. Phys. JETP **4**, 153 (1956)]; G. F. Zharkov, Zh. Eksp. Teor. Fiz. **34**, 412 (1958) [Sov. Phys. JETP **7**, 286 (1958)].