Magnetoelectric Effect in Polar Superconductors

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The question of how the lack of spatial reflection symmetry can affect properties of a superconductor is investigated. A novel magnetoelectric effect is predicted: The supercurrent in a metal of polar symmetry must be accompanied by the spin polarization of the carriers. The relevance to some known pyro- and antipyroelectric superconductors including a high-temperature system as well as the possibility of an experimental verification are briefly discussed.

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Since the discovery of optical activity at the beginning of the last century, studying parity-violating phenomena in different branches of physics has been an active field of endeavor. Yet the uncommon properties that objects possessing violated space parity could reveal are still intriguing and have not been fully explored. In this respect, the phenomenon of superconductivity in metals of polar symmetry, i.e., spontaneous breaking of the U(1) gauge invariance under the no-space-parity condition, is of the utmost relevance. The very concept of polar superconductors was introduced into physics as early as 1965 in a seminal paper by Anderson and Blount [1] in connection with the phase transformations in some intermetallic compounds. Such compounds, ferroelectric metals (e.g., V_2Hf with space group $Imm2$ [2]), were discovered afterwards. Pyroelectric metals (i.e., materials crystallizing in a polar structure) became known much later. A good example is $CeCoSi_3$, found by investigating new ternary intermetallic silicides of the general formula $RTSi_3$ (where R represents rare-earth metals and T represents transition metals), which crystallize in the $BaNiSn_3$ structure with space group $I4mm$. It behaves like a normal metal and becomes superconducting below $T_c \simeq 1.3$ K [3]. Besides that, the new family of noncentrosymmetric high-T_c superconductors $Y_{1-x}Ca_xSr_2GaCu_2O_{7\pm y}$ [4] with space group $Ima2$ has been recently brought to light and attracts increasing interest [5]. Furthermore, it should be noted that many well known high-T_c compounds contain elements of broken space parity. Thus, for example, the metallic Cu-O planes in YBCO, which the current carriers (we shall call them electrons for simplicity) are confined to, are asymmetric in that the ions surrounding such a plane from above and from below are of different charge. In fact, a Cu-O plane in YBCO is surrounded on one side by yttrium ions and on the other side by barium ones. The loss of the up-down symmetry of the immediate environment means the presence of an intracrystalline electric field threading the plane and gives rise to a spin-orbit term in the electron Hamiltonian

$$H_{SO} = \frac{\alpha}{\hbar}(\mathbf{p} \times \mathbf{c}) \cdot \boldsymbol{\sigma}, \qquad (1)$$

where $\mathbf{p}$, $\boldsymbol{\sigma}$, and $\mathbf{c}$ are, respectively, the 2D momentum, the Pauli matrices, and a unit vector along one of the inequivalent normals to the plane (for analogous reasons, the same term should be present in the electron Hamiltonian of a 3D polar metal). The term was discussed for the first time in connection with the energy spectrum of bulk [6] and surface [7] electronic states in some semiconductors. In the presence of H_{SO}, time-reversal symmetry no longer ensures the spin degeneracy of the electronic states. The states of positive and negative helicity (the projection of a spin on the $\mathbf{p} \times \mathbf{c}$ direction) acquire different energies. The kinetics of a system with lifted spin degeneracy can be expected to exhibit anomalous features. Unfortunately, the space asymmetry just described is somewhat hidden in YBCO due to the opposite orientation of the adjacent planes (from our point of view, such compounds should be termed antipyroelectric metals) and remains so far unexploited. In contrast, the mirror symmetry of ferro- and pyroelectric metals mentioned above is violated on the macroscopic level.

The purpose of the present paper is to point out a novel phenomenon which must take place in polar metals. That is, the supercurrent $\mathbf{J}_s$ induces the spin polarization $\mathbf{S}$ of the carriers in an amount proportional to $\mathbf{c} \times \mathbf{J}_s$. Here and in the following $\mathbf{c}$ is the unit vector along the polar axis. The effect is an analog of the well known magnetoelectric effect predicted by Dzyaloshinskii [8]: An applied electric field leads to the occurrence of magnetization in some antiferromagnetic insulators of low symmetry. Both effects are unrelated to dissipative processes and have a purely thermodynamic nature. Yet before we present an exact equation it seems necessary to comment on the model we are going to use throughout.

It is assumed that a crystal may be viewed as a system of conducting asymmetric and equally oriented electronic layers and that the tunneling between the layers is negligible. So we shall discuss just one layer. It is also supposed that the electron spectrum in the absence of H_{SO} and of the interparticle interaction is isotropic, $\epsilon_0(p) = (1/2m)p^2$, and that singlet s-type pairing takes

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place, i.e., the Hamiltonian has the form

$$H = \int d^2r \Big\{ \frac{\hbar^2}{2m} \nabla\psi_\gamma^+(\mathbf{r}) \cdot \nabla\psi_\gamma(\mathbf{r}) + \alpha\psi_\beta^+(\mathbf{r}) \Big(\frac{\nabla}{i} \times \mathbf{c} \Big) \cdot \boldsymbol{\sigma}_{\beta\gamma}\psi_\gamma(\mathbf{r}) + \frac{\lambda_s}{2} [\psi_\beta^+(\mathbf{r})\, g_{\beta\kappa}\psi_\kappa^+(\mathbf{r})][\psi_\delta(\mathbf{r})\, g_{\delta\gamma}\psi_\gamma(\mathbf{r})] \Big\}, \tag{2}$$

where $\hat{g} = i\sigma_2$, λ_s is the pairing coupling constant, and $\psi_\gamma(\mathbf{r})$ is the electron quantized field operator. Under these assumptions, our main result has the form

$$\mathbf{S} = \frac{1}{2} \Big(\frac{\alpha m}{p_F} \Big) \Big(\mathbf{c} \times \frac{\mathbf{V}_s}{v_F} \Big) f\Big(\frac{\alpha p_F}{\pi T} \Big). \tag{3}$$

Here α is the spin-orbit constant introduced in (1), $\mathbf{V}_s$ is the superfluid velocity density defined by the equation

$$\mathbf{V}_s = \frac{1}{2m} N_s^{(2)}(T)\, \nabla\chi, \tag{4}$$

where χ is the order parameter phase, $N_s^{(2)}(T)$ is the superfluid electron density,

$$N_s^{(2)}(T) = n_2 \frac{7\zeta(3)}{4\pi^2} \Big(\frac{|\Delta|}{T} \Big)^2, \tag{5}$$

T is the temperature, $p_F = (2m\mu)^{1/2}$ and v_F are, respectively, the Fermi momentum and velocity, $|\Delta|$ is the absolute value of the order parameter, $n_2 = (1/2\pi)p_F^2$ is the particle density, $\zeta(n)$ is the Riemann ζ function, and $f(x)$ is the function defined by

$$f(x) = \frac{8}{7\zeta(3)} \sum_{n\geq 0} \frac{x^2}{(2n+1)^3[(2n+1)^2 + x^2]}. \tag{6}$$

We use units in which Boltzmann's constant and $\hbar$ are unity. Equation (3) can be shown to be true for a 3D superconductor as well if the 3D particle density $n_3 = (1/3\pi^2)p_F^3$ is substituted for n_2 in Eq. (5).

Let us now derive Eq. (3). The one-particle Hamiltonian of the asymmetric layer reads

$$H_0 = \frac{p^2}{2m} + \alpha(\mathbf{p} \times \mathbf{c}) \cdot \boldsymbol{\sigma}. \tag{7}$$

It follows from Eq. (7) that the thermal Green's function of noninteracting particles has the form [9]

$$G_0(i\epsilon, \mathbf{p}) = \hat{\Pi}^{(+)} G_+^0(i\epsilon, p) + \hat{\Pi}^{(-)} G_-^0(i\epsilon, p), \tag{8}$$

$$G_{(\pm)}^0(i\epsilon, p) = [i\epsilon - \xi_{(\pm)}(p)]^{-1}, \quad \xi_{(\pm)}(p) = \epsilon_{(\pm)}(p) - \mu, \tag{9}$$

where

$$\epsilon_{(\pm)}(p) = \epsilon_0(p) \pm \alpha p, \tag{10}$$

and

$$\Pi_{\alpha\beta}^{(\pm)}(\mathbf{p}) = \tfrac{1}{2}[\delta_{\alpha\beta} \pm (\hat{\mathbf{p}} \times \mathbf{c}) \cdot \boldsymbol{\sigma}_{\alpha\beta}]. \tag{11}$$

The operator $\hat{\Pi}^{(\pm)}$ represents the projection onto states with a definite helicity. It is seen from Eqs. (8)–(10) that the energy surface of the normal state has two branches and that the Fermi surface represents two circles of radii $p_{(\pm)} \approx p_F(1 \mp \delta)$, where $\delta = (\alpha m/p_F)$. It is important to realize that the two branches have different densities of states at the Fermi level $N_{(\pm)} \approx (1 \pm \delta)m/2\pi$ [10].

The mean value of the spin density can be evaluated according to the general rules of quantum statistics [11]. Near the critical temperature and with no external fields, the contribution to $\mathbf{S}$ due to an inhomogeneity of the order parameter is schematically represented in Fig. 1. In the long-wavelength limit one can drop the $\mathbf{q}$ dependence of the two electron propagators $\hat{G}(i\epsilon, \mathbf{p} \pm \frac{1}{2}\mathbf{q})$ adjoined to the $\vec{\sigma}$ vertex and expand the third propagator $\hat{G}^t(i\epsilon, -\mathbf{p} + \mathbf{q}')$ in a power series in the momentum $\mathbf{q}'$. The contribution of zero order in $\mathbf{q}'$ vanishes and all terms having more than one power of $\mathbf{q}'$ can be dropped as well. With these modifications, $\mathbf{S}$ can be expressed as

$$S_i = -\frac{T}{2} \sum_{\epsilon_n} \int \frac{d\mathbf{p}\, d\mathbf{q}'}{(2\pi)^4} \mathrm{Tr}\{\sigma_i \hat{G}(i\epsilon_n, \mathbf{p}) \hat{\Delta}(\mathbf{q}' + \tfrac{1}{2}\mathbf{q}) \times \hat{G}^t(-i\epsilon_n, -\mathbf{p}) \hat{v}_j^t(-\mathbf{p}) \hat{G}^t(-i\epsilon_n, -\mathbf{p}) \hat{\Delta}^+(\mathbf{q}' - \tfrac{1}{2}\mathbf{q}) \hat{G}(i\epsilon_n, \mathbf{p})\} q_j'. \tag{12}$$

Here the superscript t denotes transposition,

$$\Delta_{\alpha\beta}(\mathbf{q}) = g_{\alpha\beta}\Delta(\mathbf{q}), \qquad \hat{g} = i\sigma_2, \tag{13}$$

is the order parameter matrix, and the velocity operator

$$\mathbf{v}(\mathbf{p}) = \frac{\mathbf{p}}{m} + \alpha\mathbf{c} \times \boldsymbol{\sigma} \tag{14}$$

as well as the usual scalar part also has a spin component. To evaluate $\mathbf{S}$, one should substitute Eqs. (7)–(10) into the right-hand side of Eq. (12) and make use of the identity

$$-g\boldsymbol{\sigma}^t g^t = \boldsymbol{\sigma}. \tag{15}$$

Then it is easy to show that

$$\int \frac{d\hat{\mathbf{p}}}{2\pi} \mathrm{Tr}\{\hat{\Pi}^{(\mu)}(\mathbf{p}) \sigma_i \hat{\Pi}^{(\nu)}(\mathbf{p}) \hat{\mathbf{v}}_j(\mathbf{p})\} q_j' = \tfrac{1}{2}(\mathbf{q}' \times \mathbf{c})_i Q_{(\mu\nu)}, \tag{16}$$

where

$$Q_{\mu\nu} = \begin{pmatrix} \frac{p}{m} + \alpha & \alpha \\ \alpha & -\frac{p}{m} + \alpha \end{pmatrix}, \tag{17}$$

and the indices μ and ν identify the branches of the

energy surface. Furthermore, it is evident that

$$\int \frac{d\mathbf{q}'}{2\pi}\,\mathbf{q}'\Delta^*\left(\mathbf{q}'-\frac{1}{2}\,\mathbf{q}\right)\Delta\left(\mathbf{q}'+\frac{1}{2}\,\mathbf{q}\right)=\frac{i}{2}\int d\mathbf{r}\,e^{-i\mathbf{q}\cdot\mathbf{r}}\{[\nabla\Delta^*(\mathbf{r})]\Delta(\mathbf{r})-\Delta^*(\mathbf{r})[\nabla\Delta(\mathbf{r})]\}, \tag{18}$$

where Δ^* denotes the complex conjugation function. As a result, going from momentum space to configuration space, we get

$$\mathbf{S}=-\frac{\Delta^2}{4}(\nabla\times\mathbf{c})T\sum_{\epsilon_n}\sum_{\mu\nu}\int_0^\infty\frac{p\,dp}{2\pi}\,\frac{Q_{(\mu\nu)}}{[(i\epsilon_n)^2-\xi^2_{(\mu)}][(i\epsilon_n)^2-\xi^2_{(\nu)}]}, \tag{19}$$

where $\epsilon_n=(2n+1)\pi T$ and n runs over all positive and negative integers. The diagonal elements of $\hat{Q}$ contribute to the second sum of Eq. (18),

$$-\frac{2\alpha m}{|\epsilon_n|^3}, \tag{20}$$

whereas the nondiagonal elements give

$$\frac{2\alpha m}{|\epsilon_n|[|\epsilon_n|^2+(\alpha p_F)^2]}. \tag{21}$$

Equation (3) may now be obtained immediately. Two remarks are in order.

(i) The value of α in polar metals and the asymmetric Cu-O layers in the high-T_c compounds is unknown at present but apparently it is not too large, being of relativistic origin. Among the substances mentioned above, the largest magnitude of α can be expected in $CeCoSi_3$, because it is mainly composed of heavy elements. The value of α in the asymmetric Cu-O layers could be noticeable as well. It is generally believed that the conduction band in these compounds is basically made up of the oxygen orbitals, and it is certainly true that the value of SO coupling in oxygen is next to nothing. This fact, however, has nothing to do with the problem—α (of the conduction band) does not depend *at all* on the SO energy of the atomic states that the conduction band is composed of. In fact, it was ascertained over a decade ago [12] that the proximity of other bands, which are built from wave functions of heavier atoms (e.g., Cu) and to which the electron transitions from the conduction band are dipole allowed, is necessary for an appreciable value of α. An important point of the theory presented in Ref. [12] is that the contribution of a given band (to the constant α of the conduction band) is proportional not only to the magnitude of the SO energy of the atomic orbitals that the band is built from, but also to the inverse square of the energy gap between that band and the conduction band. If the gap is very small on the atomic scale (Ry = 27 eV), then this factor can compensate the smallest atomic SO energy and strongly enhance α. This is likely to take place in high-T_c compounds as they exhibit several optical bands with energies in the range from midinfrared to ultraviolet [13]. Without giving any details, we mention that $\alpha p_F \sim 50$ K at $p_F/\hbar \approx 3.5\times 10^7$ cm^{-1} might be the right order-of-magnitude estimate in the case of Cu-O layers of antipyroelectric high-T_c compounds. The same could be true for $CeCoSi_3$. So one can expect the f function in Eq. (3) to be of the order of unity and $\delta\sim 10^{-3}$ at $\epsilon_F\approx 2\times 10^3$ K. The polarization per one electron can, therefore, amount to $\delta(T_c/\epsilon_F)\sim 10^{-5}-10^{-4}$ at a superfluid velocity of the order of $T_c/(mv_F)$.

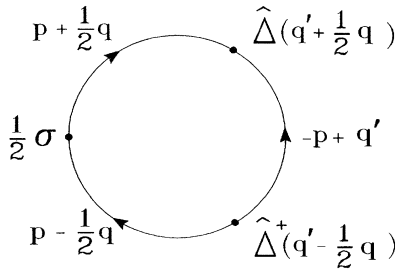

FIG. 1. Diagram of the contribution of the inhomogeneous order parameter to the magnetization.

(ii) The dirty limit, when $\alpha p_F\tau\leq 1$ and $T_c\tau\leq 1$ (τ is the elastic collision time), is likely to be more suitable for real materials. It will be considered separately.

One way of verifying the theory developed is to investigate the NMR frequency shift in a current-carrying sample. Let us suppose that a ferro- or pyroelectric superconductor is subjected to a magnetic field $\mathbf{H}_0$. Then the Knight shift, being determined by the sum of the magnetization induced by $\mathbf{H}_0$ ($\mathbf{M}_0\sim\mathbf{H}_0$) and that induced by the supercurrent ($\mathbf{M}_s\sim\mathbf{c}\times\mathbf{J}_s$), should have a term proportional to the mixed product $\mathbf{H}_0\cdot(\mathbf{c}\times\mathbf{J}_s)$, which is an odd function of the field $\mathbf{H}_0$. It is worth mentioning that the experiment should also show a positive result in antipyroelectric superconductors (at least in strongly anisotropic $Bi_2Sr_2CaCu_2O_x$, where one can neglect coherent tunneling between Cu-O planes). In this case, the NMR shifts of nuclei lying in oppositely oriented Cu-O layers will have opposite signs. So the supercurrent should induce broadening of the NMR line. Then by rotating the field $\mathbf{H}_0$ with some frequency, one can try to detect the modulation of the shift on the double frequency.

Thus we have shown that the superconducting state of parity-nonconserving materials should exhibit unusual qualities; in particular, we have demonstrated that the supercurrent in polar metals gives rise to spin magnetization. A distinctive feature of the effect is that it is odd in the crystal orientation and the current direction. The results obtained allow us to expect fairly nontrivial spin dynamics

in polar superconductors as well as in the layered antipyroelectric high-T_c compounds.

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