The type of superconductivity in Bechgaard's salts

L. P. Gor'kov
L. D. Landau Institute of Theoretical Physics, Academy of Sciences of the USSR

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If the superconductivity in Bechgaard's salts corresponds to a triplet pairing, an alternating magnetic field at the surface will excite "spin waves" in the interior of the superconductor. The detection of these waves might make it possible to experimentally resolve the nature of the superconducting pairing in these materials.

The nature of the superconducting pairing in "Bechgaard's salts" [the compounds $(TMTSF)_2X$, where $X = PF_6$, ClO_4, etc.] has yet to be resolved. Several facts do not conform to the BCS theory of superconductivity. For example, the critical temperature of the superconducting transition in these salts depends on defects and on the pressure (see the reviews in Refs. 1–3). The upper critical field along the principal axis is so high at low temperatures that the "paramagnetic limit" for *s*-pairing is violated at low temperatures.[4] Another interesting point is that the superconducting state usually arises under pressure at the boundary at which dielectric pairing in a spin density wave becomes unstable. Under these conditions, spin fluctuations might play an important role in the interaction of Cooper electrons (Ref. 5, for example).

In this paper we wish to discuss an effect which—if it were to be observed experimentally—would unambiguously demonstrate a triplet nature of the superconductivity in these compounds. We are talking about the excitation of spin waves which are associated with a rotation of the spin vector of Cooper pairs.

In triplet pairing the order parameter can be chosen in the form

$$\hat{\Delta}(\mathbf{p}) = i(\hat{\vec{\sigma}}\mathbf{d})\,\hat{\sigma}^{y} f(\mathbf{p}), \qquad (1)$$

where the vector **d** describes the spin degrees of freedom of the Cooper pair, and $f(\mathbf{p})$ is the solution of the nonlinear problem of the theory of superconductivity. The specific form of this solution is unimportant to the discussion below. When we ignore the spin-orbit interaction, the direction of the vector **d** is not fixed, as in ^{3}He. Low-lying spin modes are associated with a rotation of the spin vector. These modes are capable in principle of propagating into the interior of the superconductor. In a wave of this sort, the spin currents in the interior of the superconductor are basically cancelled by orbital currents. There is a significant magnetic field only in a screening layer, and it is here that a spin wave is excited. In particular, this process would correspond to the absorption of energy by the superconductor in the low-frequency region, $\omega \ll T_c$, at arbitrarily low temperatures.

Calorimetric measurements in these materials reveal a well-defined three-dimensional phase transition at T_c. The specific heat falls off sharply below T_c, probably in an exponential way.[1,3] The energy gap in the spectrum is determined by the quantity

$$\det\hat{\Delta}(\mathbf{p}) = \mathbf{d}^2 f(\mathbf{p}). \qquad (2)$$

On the other hand, although Bechgaard's salts do belong to the triclinic system, they have an inversion center. For triplet pairing we would then have

$$f(-\mathbf{p}) = -f(\mathbf{p}). \qquad (3)$$

Condition (3) is consistent with an activation behavior of the specific heat in the superconducting phase at low temperatures, since the Fermi surface for these compounds consists of two open regions. However, an activation law for the specific heat does impose a condition in (2): $\mathbf{d}^2 \neq 0$.

Accordingly, an equilibrium state in the superconducting phase, if it corresponds to a triplet pairing, can be described by a real spin vector in (1). Its orientation at equilibrium will of course be fixed by the low energy of the magnetic anisotropy.

Let us assume that an alternating magnetic field of frequency $\omega \ll T_c$ is applied to the surface of the superconductor. In the Meissner layer (at the penetration depth δ) the magnetic field excites corrections of the following type to the order parameter:

$$\mathbf{d}_1 - \mathbf{d}_1^* = 2i\varphi\mathbf{d}; \quad (\mathbf{d}_1 + \mathbf{d}_1^*)/2|\mathbf{d}| = \mathbf{s},$$

where $\mathbf{s}\perp\mathbf{d}$. Actually, there are no phase oscillations, since the condition of electrical neutrality would reduce such oscillations to high-frequency plasma modes. Rotations of the vectors **d** and **s** in the absence of a spin-orbit interaction arise from the paramagnetic terms in the electron energy, $\mu_B(\hat{\vec{\sigma}}\mathbf{H})$. The rest of this paper is a derivation of equations for the vector **s** and a solution of the electromagnetic problem

$$\operatorname{curl}\mathbf{B}=\frac{4\pi}{c}\mathbf{j};\quad \mathbf{j}=\mathbf{j}_{\text{orb}}+\mathbf{j}_{\text{spin}}. \tag{4}$$

In (4) we have $\mathbf{j}_{\text{orb},i}=n^s_{ik}(\nabla\varphi-2eA/c)_k$, since organic superconductors are type II superconductors; i.e., they are described by a local electrodynamics.

We have derived equations for the vector **s** and an expression for $\mathbf{j}_{\text{spin}}$ at $T=0$; we will reproduce only the results here:

$$\left(\overline{v_iv_k}\,\frac{\partial^2}{\partial x_i\partial x_k}-\frac{\partial^e}{\partial t^2}\right)\mathbf{s}=2\mu_B[\dot{\mathbf{B}}\times\mathbf{n}], \tag{5}$$

$$\mathbf{j}_{\text{spin}}\simeq\mu_B c\nu(E_F)\frac{\partial}{\partial t}\operatorname{curl}[\mathbf{s}\times\mathbf{n}]. \tag{6}$$

Here and above, $\mathbf{n}=\mathbf{d}/|\mathbf{d}|$; $\nu(E_F)$ is the state density (per spin); $\overline{v_iv_k}=\int v_F^{-1}v_iv_k dS/\int v_F^{-1}dS$; and $n^s_{ik}=(2\pi)^{-3}\,\overline{v_iv_k}$.

As we have already mentioned, $(\text{TMTSF})_2\text{X}$ crystals belong to the triclinic system, which is close to the monoclinic system, where the principal directions are the axes of the conductivity tensor and therefore of the tensor n^s_{ik}. In this approximation we have

$$n^s_{ik}=n^s_i\,\delta_{ik},\quad \overline{v_iv_k}=\overline{v_i^2}\delta_{ik}.$$

Solving electrodynamic problem (4) with (5), (6) requires boundary conditions of some sort on the vector **s**. We have used $s(z=0)=0$, but the magnitude of the effect depends only weakly on the choice of boundary conditions. The magnetic field associated with the spin wave far from the surface $(z\gg\delta_z)$ is of course weak:

$$H_y^{(1)}(z)\simeq\frac{4\pi\chi i\sqrt{\overline{v_z^2}}\,H_y(0)}{\omega\delta_z}\;\frac{\omega^4\exp\left(i\omega z/\sqrt{\overline{v_z^2}}\right)}{(\omega^2+\overline{v_z^2}/\delta_z^2)^2}. \tag{7}$$

In other words, at $\omega\delta_z/\sqrt{\overline{v_z^2}}\sim 1$ we have $H_y^{(1)}(z)\sim\chi H_y(0)$ in order of magnitude, where $H_y(0)$ is the field at the surface. (For Bechgaard's salts, we have $\chi\sim10^{-6}$–10^{-7}.)

It appears to us the the propagation of a spin wave through a sample might nevertheless be detected comparatively easily by using two identical resonators separated by the material under study. A favorable circumstance here is that the electric vector in the wave is weak in comparison with the magnetic vector, $E_x^{(1)}(z)\sim(v/c)H_y^{(1)}(z)$, as is required by the condition that the surface impedance at the surface of the superconductor must be low.

The magnitude of the dimensionless combination $\omega\delta_z/v\sim(\omega/T_c)(\delta_z/\xi_0)\sim(\kappa\omega/T_c)$ can change significantly, remaining in adherence with the condition $\omega\ll T_c\,(\kappa\gg1)$. At very low frequencies, the spin-orbit interaction must be taken into account. That interaction fixes the threshold frequency for the excitation of spin waves. The strength of this interaction can be estimated from data[6] on the antiferromagnetic resonance frequency in an antiferromagnetic phase. We then find the frequency interval in which our equations hold:

$$10^{-2}\, T_c \ll \omega \ll T_c \,.$$

In summary, the observation of spin waves in the superconducting phase of Bechgaard's salts would be a qualitative effect which could unambiguously identify a triplet nature of the superconductivity in these salts.

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