Unusual Transport Effects in Anisotropic Superconductors

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We show that scattering processes in anisotropic superconductors have some unexpected asymmetries when the normal-state phase shift is neither small nor resonant. The scattering rate is not symmetric about the Fermi surface, which gives rise to large thermoelectric effects. For states with gaps that have nontrivial phase variations over the Fermi surface, certain components of transport coefficient tensors can be finite even though they vanish in the normal state.

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In an attempt to understand measurements of transport properties of superconducting heavy-electron systems,[1] a number of authors have considered scattering of quasiparticles by nonmagnetic impurities in anisotropic superconductors. These studies show that, in marked contrast to what is found for a BCS superconductor, the mean free path behaves in very different ways depending on the phase shift of the impurity. For small phase shifts, the scattering rate in superconducting states with nodes in the energy gap is proportional to a power of the temperature at temperatures well below the superconducting transition temperature, T_c, while for resonant scattering ($\delta_N = \pm\pi/2$) the temperature dependence is much weaker.[2] This effect was first pointed out by Pethick and Dines,[3] and detailed calculations that take into account pair breaking were performed by Hirschfeld, Vollhardt, and Wölfle[4] and others.[5-8] The experimental data[8] appear to indicate that the phase shift is probably close to $\pi/2$, but at present it is not possible to make precise statements because the nature of the superconducting state is not well understood.

In this Letter we discuss two classes of effects which can occur when the normal-state phase shift is neither small nor completely resonant. The first, a quasiparticle-quasihole asymmetry on energy scales of order $k_B T_c$, gives rise to an anomalously large thermoelectric effect. The second, associated with order parameters with a nontrivial phase variation over the Fermi surface, as, for example, in the Anderson-Brinkman-Morel p-wave state, produces angular asymmetries in the scattering cross section. As a consequence, some components of transport coefficients that vanish in the normal state are finite in the superconducting state. Which particular transport coefficients acquire infinite values depends on the angular symmetry of the order parameter, and therefore experimental observation of them would provide a way of distinguishing among different superconducting states. The effects discussed here might also prove useful in elucidating the nature of the superconducting states in the high-T_c materials.

To show how the effects arise, we consider scattering of quasiparticles in a superconductor by an impurity. For simplicity we assume that the scattering is only s wave, and that the concentration of impurities is sufficiently low that pair-breaking effects may be ignored. The amplitude for a single impurity to scatter a quasiparticle from a state with momentum $\mathbf{p}$ to one with momentum $\mathbf{p}'$ is obtained by performance of a Bogoliubov transformation on the scattering amplitude in the superconductor for normal-state quasiparticles and quasiholes, and is given by[3,9]

$$t^s_{\mathbf{p}'\mathbf{p}}(E) = u^\dagger_{\mathbf{p}'} t_{11}(E) u_{\mathbf{p}} + u^\dagger_{\mathbf{p}'} t_{12}(E) v_{\mathbf{p}} + v^\dagger_{\mathbf{p}'} t_{21}(E) u_{\mathbf{p}} + v^\dagger_{\mathbf{p}'} t_{22}(E) v_{\mathbf{p}}. \tag{1}$$

Here t_{ij}, $i=1,2$, is the scattering amplitude in normal-state quasiparticle-quasihole space, with $i=1$ referring to quasiparticles and $i=2$ to quasiholes, $u_{\mathbf{p}}$ and $v_{\mathbf{p}}$ are the usual coherence factors, and for simplicity we have suppressed spin indices. The scattering amplitude is especially simple for states with order parameters which are odd under the replacement of $\mathbf{p}$ by $-\mathbf{p}$, or under reflection of $\mathbf{p}$ in some plane. All the anisotropic states we shall consider in detail in this Letter, namely the axial (ABM) and polar p-wave states and the d-wave state with an order parameter proportional to $\sin\theta\cos\theta e^{i\phi}$, fall into these classes. These states are often referred to as unconventional superconductors, in that the crystal symmetry of the order parameter is lower than that of the normal metal. Here θ and ϕ are the polar coordinates of $\hat{p}$. One finds $t_{12} = t_{21} = 0$ and

$$t_{11}(E) = -t^*_{22}(-E) = -\frac{1}{\pi N(0)} \frac{\tan\delta_N}{1 - i\tan\delta_N g(E)}, \tag{2}$$

where

$$g(E) = \frac{i}{\pi} \int \frac{d\Omega_{\mathbf{p}}}{4\pi} \int_{-E_0}^{E_0} d\xi_{\mathbf{p}} \frac{E}{E^2 - E^2_{\mathbf{p}}}. \tag{3}$$

$N(0)$ is the density of states of one spin in the normal state and δ_N is the normal-state phase shift. E_0 is a cutoff energy, $\Delta \ll E_0 \ll E_F$, with Δ the maximum value of the gap as a function of angle on the Fermi surface and E_F the Fermi energy. The quantity $E_\mathbf{p} = (\xi_\mathbf{p}^2 + |\Delta_\mathbf{p}|^2)^{1/2}$ is the quasiparticle energy in the superconductor, $\xi_\mathbf{p}$ is the normal-state quasiparticle energy, and $\Delta_\mathbf{p}$ is the gap as a function of direction on the Fermi surface. For simplicity we consider only unitary states, for which the gap is independent of spin.

The observation which is central to all the effects we shall discuss below is that $g(E)$ has both a real part, proportional to the density of states in the superconductor, which is an even function of E, and an imaginary part which is an odd function of E. The latter vanishes for energies in excess of Δ, but is finite below Δ. For small δ_N, $t_{11}(E)$ approaches $-t_{22}(E)$, while for $\delta_N = \pm\pi/2$, $t_{11}(E)$ is equal to $t_{22}(E)$. On the other hand, for other values of the phase shift the relationship between $t_{11}(E)$ and $t_{22}(E)$ is more complicated, since the real parts of the denominators in t_{11} and t_{22} [Eq. (2)] are $1+\tan\delta_N \times \mathrm{Im}g(E)$ and $1-\tan\delta_N \mathrm{Im}g(E)$, respectively. Physically, the difference is due to the fact that $t_{11}(E)$ is a particle amplitude, while $t_{22}(E)$ is a hole amplitude, and the basic interaction between an impurity and a particle is the negative of that between the impurity and a hole. The difference between the amplitudes reflects the physical difference between attractive interactions, which tend to form bound states, and repulsive ones, which do not. In the case of scattering processes, this difference is apparent only if the potential is sufficiently strong that the Born approximation is inadequate.

The squared modulus of the scattering amplitude summed over final spin states and averaged over initial spin states is given by

$$\langle |t^s_{\mathbf{p}'\mathbf{p}}|^2\rangle = \tfrac{1}{2}|t_N|^2\{[a(1+\xi_\mathbf{p}\xi_{\mathbf{p}'}/E_\mathbf{p}E_{\mathbf{p}'}) + b(\xi_\mathbf{p}/E_\mathbf{p}+\xi_{\mathbf{p}'}/E_{\mathbf{p}'}) + \mathrm{Re}[\tfrac{1}{2}c\,\mathrm{tr}(\hat{\Delta}_\mathbf{p}\hat{\Delta}^\dagger_{\mathbf{p}'}/E_\mathbf{p}E_{\mathbf{p}'})]\}, \tag{4}$$

where

$$a = (|t_{11}|^2 + |t_{22}|^2)/2|t_N|^2,$$

$$b = (|t_{11}|^2 - |t_{22}|^2)/2|t_N|^2,$$

and $c = t_{11}t_{22}^*/|t_N|^2$ and $|t_N| = (\sin\delta_N)/\pi N(0)$. For the anisotropic states that we consider in this paper, which all have gaps that are odd under the parity transformation or a reflection, the relaxation time is given simply by

$$\frac{1}{\tau_\mathbf{p}} = \frac{1}{\tau_N}\left(a + b\frac{\xi_\mathbf{p}}{E_\mathbf{p}}\right)\frac{N_s(E_\mathbf{p})}{N(0)}, \tag{5}$$

where $N_s(E_\mathbf{p})$ is the density of quasiparticle states in the superconductor, and τ_N is the normal-state relaxation time.

A surprising feature of the relaxation time (5) is that it contains a term proportional to $\xi_\mathbf{p}$, and therefore it is not symmetric about the Fermi surface. For energies less than Δ, Img is comparable to unity, and therefore b typically has a magnitude $\sin(2\delta_N)$. The existence of such asymmetries has previously been pointed out by Pethick and Dines,[10] and by Monien *et al.*[7] who took them into account in calculations of the ultrasonic attenuation. In metals there are, of course, other asymmetries of the relaxation time about the Fermi surface, due to variations of the normal-state density of states and the matrix elements, but these are generally on an energy scale E_F. In superconductors the effects of the latter asymmetries are generally small, and we have implicitly neglected them in the calculation described here.

The asymmetry about the Fermi surface has a number of consequences, the first of which is that in the calculation of transport coefficients it is generally necessary to solve a pair of coupled equations for the parts of the distribution function even and odd in $\xi_\mathbf{p}$.[7,11] This is in contrast to what is the case for a normal Fermi liquid at low temperatures, where the collision integral does not mix odd and even terms, and therefore the equations for the odd and even parts of the distribution function are uncoupled. A second, and more interesting, effect is that there are large thermoelectric coefficients. The application of a temperature gradient to a superconductor drives a normal current, given by $j_n^i = -L_{ij}\nabla_j T$. The coefficient L_{ij} vanishes at $T=0$, because the values of $\xi_\mathbf{p}$ for which there are thermally excited quasiparticles vanish as $T\to 0$, and at $T=T_c$ because the asymmetries are present only for energies less than the maximum value of the gap. The Boltzmann equation may be solved exactly for this problem,[11] and in Fig. 1, we show results for L_{xx} in the d-wave state discussed above, where the x axis is perpendicular to the symmetry axis of the state. The effect changes sign under reversal of the sign of δ_N. In

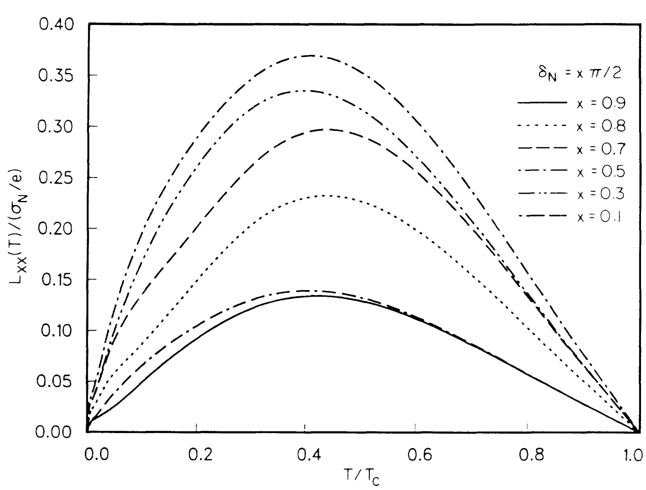

FIG. 1. Thermoelectric coefficient I_{xx} as a function of temperature for the d-wave state described in the text.

these calculations we used a simplified expression for the gap first suggested by Wölfle and Koch.[12] Even for phase shifts of about $0.9\pi/2$, a value deduced from specific-heat measurements for UBe_{13},[8] the coefficient L can be as large as $0.1\sigma_N/e$, where $\sigma_N = \frac{2}{3}e^2N(0)v_F^2\tau_N$ is the normal-state conductivity. In ordinary isotropic superconductors L is typically of order $(\sigma_N/e)(T_c/T_F)$. Since T_c/T_F for ordinary superconductors is typically of order 10^{-4}–10^{-5}, one would therefore expect the thermoelectric coefficient for heavy-electron compounds to be $\sim 10^3$–10^4 times larger than that for ordinary superconductors, for materials with comparable values of the normal-state electrical conductivity.[13]

Thermoelectric effects in superconductors cannot be detected in the same way as in normal metals, because the supercurrent shorts out any potential differences that develop, and therefore new techniques were developed for superconductors.[14] Experiments have been performed with use of a number of these, but the theoretical interpretation of the results is not always clear. Measurement of the charge imbalance induced by a temperature gradient close to the boundary of a superconductor appears to be the cleanest of these experiments, and such measurements for Al give results in good agreement with the theoretical predictions.[15] It would be of great interest to perform such experiments for heavy-fermion superconductors, but fabrication of the necessary samples and contacts is a challenging problem.

Another effect of the asymmetry of the scattering rate about the Fermi surface is that modulation of the temperature in a spatially homogeneous but time-dependent way will give rise to charge-imbalance voltage between the normal and superconducting components, an effect which can in principle be measured by tunneling techniques. We have not made detailed calculations of this effect, but we expect the voltage to be of order $\delta V \sim \omega\tau_N k_B \delta T/e$, where δT is the amplitude of the temperature modulation and ω its angular frequency. Rough estimates suggest that the effect will be difficult to detect experimentally.

Another type of asymmetry arises from the last term in Eq. (4) for the scattering amplitude, if the gap has nontrivial phase variations over the Fermi surface as, for example, in the ABM state and the d-wave state we consider, for which the gap is proportional to $e^{i\phi}$, where ϕ is the azimuthal angle of $\hat{p}$ with respect to the symmetry axis of the state. The polar state, on the other hand, has no such phase variations. The scattering probability then contains a term proportional to $\mathrm{Im}(t_{11}t_{22}^*) \times \sin(\phi-\phi')$, which is odd under reversal of the sign of $\phi-\phi'$. Physically one may regard the effect as being due to angular momentum of pairs being transferred to quasiparticles during the scattering event. More formally, the basic origin of this term is the breaking of time-reversal invariance because of the existence of a condensate of pairs with finite angular momentum.

The angular asymmetry gives rise to qualitatively new effects. In the ABM state one finds that in a thermal-conduction experiment the heat current $\mathbf{j}_E$ is not parallel to the temperature gradient ∇T, even though on the grounds of crystal symmetry alone one would expect it to be so. The thermal conductivity is therefore a tensor, K_{ij}. We have calculated K_{ij} starting from the quasiparticle Boltzmann equation.[11] It is interesting that the angular asymmetry occurs in what may be called the "in-scattering" term in the Boltzmann equation (a vertex correction in field-theoretic calculations), and it is therefore not present in the relaxation-time approximation. In Fig. 2 we show the results of calculations of K_{xy}/K_{xx} for the ABM state. This quantity is equal to the tangent of the angle between the heat current and the temperature gradient in the plane perpendicular to the symmetry axis of the state, and one sees from the figure that it can be as high as 0.05 rad for phase shifts in the vicinity of $\pi/4$ at temperatures of order $T_c/4$. However, if the phase shift is close to $\pi/2$, the effect is much reduced. The effect changes sign on reversal of the sign of δ_N. The coefficient K_{yx} is also nonzero, and is equal to $-K_{xy}$ as a consequence of the Onsager relations.[16] K_{xy} vanishes for the d-wave state, since the gap has a factor $\sin\theta\cos\theta$, where θ is the polar angle, and contributions from positive values of θ cancel those from negative values.

The viscosity and the thermoelectric coefficient can also have additional components. For the d-wave state with the gap proportional to $\sin\theta\cos\theta e^{i\phi}$, one finds that the viscosity component $\eta_{xz,yz}$ and the ones related to it by symmetry are nonzero, whereas they vanish for the ABM state. The coefficient L_{xy} of the thermoelectric tensor is finite for that ABM state, but zero for the d-wave state. New components of transport coefficients occur only if the parity of the gap is the same as that of

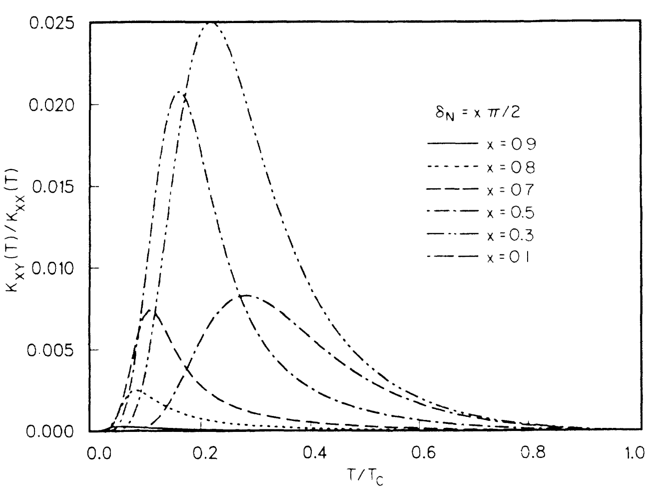

FIG. 2. K_{xy}/K_{xx} for the ABM state as a function of temperature.

the relevant current entering the transport coefficient. The heat current and the electrical current have odd parity, and therefore the thermal conductivity and thermoelectric coefficient can have additional components for p-wave states but not for d-wave ones. The conclusion for the viscosity is the opposite of this, since the momentum flux has even parity. Experimental observation of new components of transport coefficients would provide conclusive evidence for the existence of unconventional superconducting states with nontrivial phase variations over the Fermi surface, and would also determine the parity of the gap.

The calculations above give further evidence for the richness of the apparently simple process of impurity scattering in anisotropic superconductors. In the calculations we have neglected pair breaking, but this may be taken into account straightforwardly. Asymmetries about the Fermi surface can also occur in anisotropic conventional superconductors, in which the crystal symmetry of the order parameter is the same as that of the Fermi surface, when one goes beyond the Born approximation. These will be discussed in a separate paper.[17] The angular asymmetry of the scattering amplitude will also lead to anisotropies in the mobility of ions in superfluid ^{3}He.

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[1]For a review of measurements of transport coefficients in heavy-electron systems, see J. Flouquet *et al.*, J. Magn. Magn. Mater. **54-57**, 322 (1986); A. Sulpice, P. Gandit, J. Chaussy, J. Flouquet, D. Jaccard, P. Lejay, and J. L. Tholence, J. Low Temp. Phys. **62**, 39 (1986).

[2]The scattering is a periodic function of δ_N with period π, and therefore results for phase shifts outside the range $-\pi/2 \leq \delta_N \leq \pi/2$ may be simply obtained from results for $|\delta_N| \leq \pi/2$. Consequently we shall consider only phase shifts whose magnitude is less than or equal to $\pi/2$.

[3]C. J. Pethick and D. Pines, Phys. Rev. Lett. **57**, 118 (1986).

[4]P. Hirschfeld, D. Vollhardt, and P. Wölfle, Solid State Commun. **59**, 111 (1986).

[5]K. Scharnberg, D. Walker, H. Monien, L. Tewordt, and R. A. Klemm, Solid State Commun. **60**, 535 (1986).

[6]S. Schmitt-Rink, K. Miyake, and C. M. Varma, Phys. Rev. Lett. **57**, 2575 (1986).

[7]H. Monien, K. Scharnberg, L. Tewordt, and D. Walker, Solid State Commun. **61**, 581 (1987).

[8]H. R. Ott, E. Felder, C. Bruder, and T. M. Rice, Europhys. Lett. **3**, 113 (1987).

[9]B. Arfi and C. J. Pethick, Phys. Rev. B (to be published).

[10]C. J. Pethick and D. Pines, in Festschrift for V. L. Ginzburg, edited by E. Fainberg and L. Keldysh (to be published).

[11]B. Arfi, H. Bahlouli, and C. J. Pethick, to be published.

[12]P. Wölfle and V. E. Koch, J. Low Temp. Phys. **30**, 61 (1978).

[13]Since we first submitted this Letter, we have received a paper by P. J. Hirschfeld, Phys. Rev. B (to be published), who makes similar conclusions. In addition, Hirschfeld considered effects in the thermoelectric coefficient of the anisotropy of the Fermi surface and possible ways of detecting thermoelectric effects.

[14]D. J. Van Harlingen, Physica (Amsterdam) **109& 110 B+C**, 1710 (1982).

[15]H. J. Mamin, J. Clarke, and D. J. Van Harlingen, Phys. Rev. B **29**, 3881 (1984).

[16]When applying the Onsager relations, one must remember that the direction of the angular momentum of the pairs is reversed under the operation of time reversal. See, e.g., L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part I* (Pergamon, Oxford, 1980), p. 367.

[17]H. Bahlouli, H. Monien, and C. J. Pethick, to be published.