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# Thin films of anisotropic superconductors

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The effects of boundary scattering in $p$- and $d$-wave thin ($d \lesssim \xi$) superconducting films are studied. Even for specularly reflecting walls, the transition temperature of anisotropic superconductors is monotonically depressed as the thickness decreases and does not exhibit the oscillations characteristic of an ordinary $s$-wave (isotropic) superconductor. In the presence of a rough boundary, diffusive scattering dramatically reduces $T_c$, resulting in a critical thickness below which the film remains normal. In the $p$-wave (odd-parity) case there is a critical roughness above which a finite density of states appears at the Fermi level; $d$-wave (even-parity) superconducting films are always gapless.

The discovery of superconductivity in heavy-fermion compounds[1-3] (e.g., $CeCu_2Si_2$, $UBe_{13}$, $UPt_3$) has resulted in intense activity concerning the nature of superconductivity in these materials. Much of the attention has been centered on the question of which mechanism causes the superconducting instability; this is still a very controversial issue.[4-9] Regardless of what the actual mechanism is, experiments on the temperature dependence of the ultrasonic attenuation,[10,11] specific heat,[12] thermal conductivity,[13] and the local moment relaxation rate[14] suggest that, at least in the uranium compounds, the superconducting state is anisotropic with the gap parameter vanishing along lines or at points on the Fermi surface. This is indicative of pairing in a state different from the one found in ordinary superconductors.

In this paper I calculate the transition temperature of $p$- ($L=1,\ S=1$) and $d$-wave ($L=2,\ S=0$) superconductors in the thin-film geometry ($d \lesssim \xi$) with rough boundaries. I consider these states as examples of odd- and even-parity states which form a proper basis for classification of superconductors with strong spin-orbit coupling. This classification has been investigated by Anderson,[15] Volovik and Gorkov,[16] and Blount.[17] The results presented here are qualitatively correct for an arbitrary odd- (even-) parity state which is a mixture of the $p$- ($d$-) wave and higher harmonics. The main point of the paper is to emphasize the qualitative effect of boundary scattering in films of anisotropic (which I define as mixtures of $L \geqslant 1$ states) superconductors, and the differences with the standard isotropic ($L=0,\ S=0$) case. These differences are so remarkable that the sensitivity of anisotropic superconductors to boundary scattering could be used to determine whether in heavy-fermion materials we are indeed dealing with some exotic form of superconductivity.

Near a planar wall, an anisotropic order parameter has to meet the boundary condition which specifies that the orbital angular momentum of the Cooper pairs has to point along the direction perpendicular to the wall.[18] In films much thicker than the coherence length this could lead to textural effects, as in superfluid $^3$He, where the bulk phase is modified near a solid wall in order to satisfy the boundary condition.[18] When the thickness is comparable to or less than the coherence length, however, only the $m_L = \pm L$ components of the order parameter can be different from zero[19] and the superconducting state in the film can, in principle, be different from that in the bulk. In this representation $\Delta(\hat{k})$ is spanned by $\hat{k}_x$ and $\hat{k}_y$ for a $p$-wave superconductor, and by $\hat{k}_x^2 - \hat{k}_y^2$ and $2\hat{k}_x\hat{k}_y$ for the $d$-wave case. Furthermore, the BCS free energy of two-dimensional superconductors is minimized if the gap parameter is isotropic in the $x$-$y$ plane.[20] Therefore, I will consider only those forms of the order parameter in which both components $m_L = -L$ and $+L$ contribute with equal weight (all such phases are degenerate as far as the BCS form of the free energy is concerned). Then $\mathrm{Tr}\Delta^+(\hat{k})\Delta(\hat{k})$ equals $\Delta^2\sin^2\theta_\nu$ and $\Delta^2\sin^4\theta_\nu$ independent of $\hat{k}$ in the $p$- and $d$-wave state, respectively, where $\nu$ denotes the principal quantum number associated with quantization in the $z$ direction.

I will first consider the case of an ideal boundary when the scattering off the surface is purely specular. Let me assume that the electronic wave functions in the $z$ direction can be replaced by those of a particle moving in an infinite square-well potential, i.e., $u_\nu(z) = (2/d)^{-1/2}\sin[(\pi\nu/d)z]$, $\nu = 1, 2, \ldots$. While this is a bold assumption, the self-consistent calculations of Blatt and Thompson[21] for singlet superconducting films demonstrate its validity for all but very small thicknesses (comparable to the interparticle spacing). The Fermi sphere of the bulk system now degenerates into a set of Fermi circles given by the intersections of the chemical potential with "subbands" of different $\nu$. One can then write the Gorkov equations for this system by projecting the normal and anomalous Green's functions onto the above set of single-particle states; similarly the gap equation can be obtained.[22] Taking the standard forms for the $p$- and $d$-wave model potentials, the equation for $T_c$ reads

$$1 = -\frac{3}{2}\frac{\pi\lambda}{k_F d}\left(\sum_{\nu}^{\nu_c}\sin^2\theta_\nu\right)\ln\left(\frac{T_c^0}{T_c}\exp(1/\lambda)\right) \quad p \text{ wave}, \tag{1}$$

$$1 = -\frac{15}{8}\frac{\pi\lambda}{k_F d}\left(\sum_{\nu}^{\nu_c}\sin^4\theta_\nu\right)\ln\left(\frac{T_c^0}{T_c}\exp(1/\lambda)\right) \quad d \text{ wave}. \tag{2}$$

Here $\sin^2\theta_\nu = (1-\nu^2/\nu_0^2)$, $\nu_o^2 = 2md^2\mu/\pi^2$, and $\nu_c$ is the largest integer smaller than $\nu_0$. The chemical potential $\mu$ is consistently determined for every thickness.[23]

The results for $T_c/T_c^0$ ($T_c^0$ is the bulk transition temperature) as a function of $k_F d$ are plotted in Figs. 1(a) ($p$ wave) and 1(b) ($d$ wave) ($\Gamma = 0.0$ curves). $\lambda$ was taken to be $\frac{1}{3}$, as it seems appropriate for heavy-fermion superconductors.[4,8] For $k_F d \lesssim 10$ one should not take the results too seriously since the square-well model breaks down for very

 

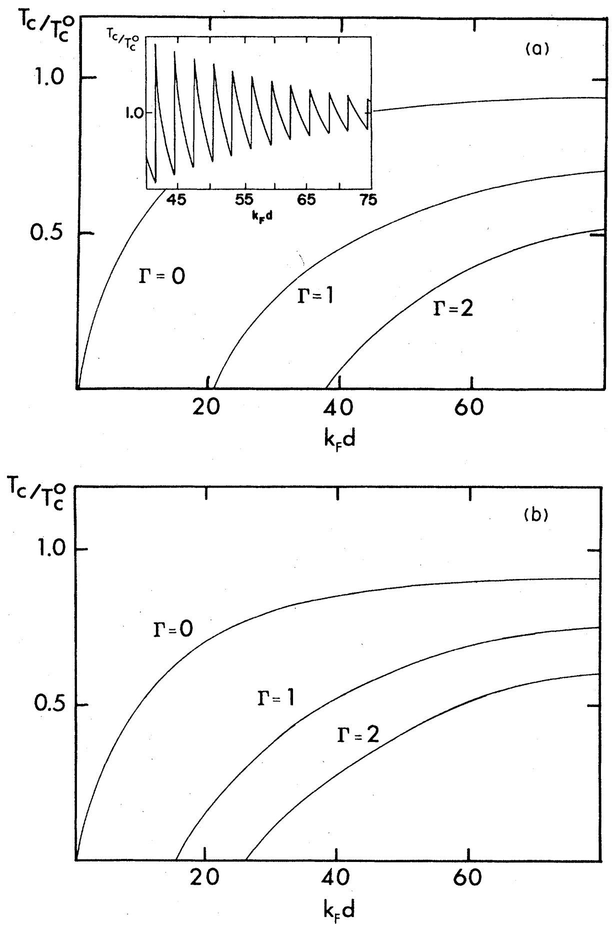


FIG. 1. (a) Variation of the transition temperature with thickness in the $p$-type superconducting film. Surface roughness is measured in units determined by setting $H=k_F^{-1}$ and $a=k_F^{-1}$. The inset schematically shows the same quantity in an ordinary superconductor. (b) Same as (a) for the $d$-wave superconductor.

thin films.[23] Even for an ideal boundary $T_c$ in both $p$- and $d$-wave cases goes down with thickness (unlike the $s$-wave case, where the average $T_c$ remains unchanged[24]) and does not exhibit the oscillations characteristic of quantum size effects in ordinary superconductors[23] [inset of Fig. 1(a)]. In fact, these oscillations, which are due to discontinuous changes in the normal density of states, can only be present in an $s$-wave superconductor.[25] For any $L\neq 0$ the effective pairing potential has nodes at the poles of the Fermi sphere, which assures that the oscillations are not present; this remains true even with the spin-orbit coupling and crystal symmetries of the heavy-fermion superconductors included, as long as one of the crystalline axes is perpendicular to the film. Experimentally, quantum oscillations in $T_c$ are quite prominent in ordinary superconductors,[26] and failure to observe them in thin films of heavy-fermion superconductors would be a strong argument in support of their exotic nature.

It is well known that even nonmagnetic scattering acts as a pair breaker in anisotropic superconductors.[27] One can therefore expect that surface roughness may influence superconductivity in our films. In order to investigate the effects of surface roughness I assume that the thickness of the film is not constant but is some random function of position in the $x$-$y$ plane, i.e., $d(x,y)=d+w(x,y)$, where $w(x,y)$ is a Gaussian random function satisfying $\langle w(x,y)\rangle=0$ and

$$\langle w(x,y)w(x',y')\rangle = H^2a^2\delta(x-x')\delta(y-y') \ .$$

$H$ and $a$ measure the average height and "scattering length" of surface irregularities, respectively. For $w(x,y) << d$ one can formulate the perturbation theory, quite analogous to the Abrikosov-Gorkov treatment of superconducting alloys, and find the self-energy corrections to the normal and anomalous Green's functions due to diffusive scattering off the boundaries.[28] These self-energy corrections turn out to depend on the subband index $\nu$, which is not surprising, since those electrons moving in directions close to the $z$ axis experience more scattering than those moving approximately parallel to the $x$-$y$ plane. Using standard procedures[29] the self-consistent equations for the gap parameter and the self-energy in the $p$-wave case can be written as[30]

$$\tilde{\omega}_\nu = \omega + \Gamma_\nu \sum_{\nu'} \frac{\nu'^2 \tilde{\omega}_{\nu'}}{(\tilde{\omega}_{\nu'}^2 + \Delta^2 \sin^2\theta_{\nu'})^{1/2}} \ , \tag{3}$$

$$1 = \frac{3}{2} \frac{\pi\bar{\lambda}}{k_F d} \pi T \sum_{\nu} \sum_{\tilde{\omega}} \frac{\sin^2\theta_\nu}{(\tilde{\omega}_\nu^2 + \Delta^2 \sin^2\theta_\nu)^{1/2}} \ . \tag{4}$$

In the above

$$\Gamma_\nu = \frac{\pi^4}{2md^2}(H^2a^2/d^4)\nu^2 \ .$$

Similar equations hold for a $d$-wave superconductor. These equations contain, in principle, all the information about an anisotropic superconductor in the presence of a rough boundary.

To find $T_c$, Eq. (4) is expanded assuming small $\Delta$. This leads to the following expression:

$$\ln\frac{T_c}{T_c'} = -\left\langle \Psi\left(\frac{1}{2} + \frac{\Gamma\cos^2\theta_\nu}{2\pi T_c}\right)\right\rangle + \Psi\left(\tfrac{1}{2}\right) \ . \tag{5}$$

$$\Gamma = \frac{\pi^4}{2md^2}(H^2a^2/d^4)\frac{\nu_c(\nu_c+\frac{1}{2})(\nu_c+1)}{3}\nu_0{}^2 \ ,$$

$\langle \ldots \rangle$ stands for

$$\textstyle\sum_\nu \sin^2\theta_\nu(\ldots)/\sum_\nu \sin^2\theta_\nu$$

and

$$\textstyle\sum_\nu \sin^4\theta_\nu(\ldots)/\sum_\nu \sin^4\theta_\nu$$

in the $p$- and $d$-wave case, respectively, $\Psi$ is the digamma function, and $T_c'$ is the transition temperature for a given thickness in the ideal boundary case. Note that Eq. (5) does not have universal character (as in a uniform pair-breaking field), so that boundary roughness affects $p$- and $d$-wave superconducting films differently.

To plot the results for $\Gamma\neq 0$ in Fig. 1 I have used $m^*/m=200$, $k_F=1.6$ A$^{-1}$, and $T_c^0=0.5$ K as reasonable parameters for heavy-fermion superconductors.[2] The most prominent feature is the existence of a critical thickness (for a specified surface roughness) below which superconductivity vanishes. For the same surface scattering this thickness is larger in the $p$-type superconducting film; therefore the triplet state ($L=1$, $S=1$) is more sensitive to diffusive surface scattering. This is true in general: For the same $T_c^0$ superconducting films in higher $L$ states will be less sensitive to boundary roughness. In order to see this, we determine the critical thickness from Eq. (5). Expanding around $T_c \rightarrow 0$ one finds

$$\Gamma^{\rm crit} = \pi T_c'/2\gamma\eta \ , \tag{6}$$

where $\gamma$ is Euler's constant and $\ln\eta = \langle \cos^2\theta_\nu \rangle$. Equation (6) is an implicit equation for $d^{\rm crit}$ since $T_c'$ also depends on the thickness, and in principle it is necessary to find the solution numerically. However, when $d^{\rm crit}$ is not too small, so that $T_c' \cong T_c^0$, one can show that $d^{\rm crit} \cong 0.75\eta\Gamma\xi_0$, where $\xi_0$ is the BCS coherence length and $\Gamma$ is in the units of atomic roughness ($H = k_F^{-1}$, $a = k_F^{-1}$). It is clear that for smaller $\eta$ the critical thickness gets smaller also. In the $d$-wave superconducting film the gap parameter varies across different subbands as $\sin^2\theta_\nu$, and the average in Eqs. (5) and (6) weighs more than subbands with lower $\nu$, where the influence of surface scattering is small; in the $p$-wave case the $\sin\theta_\nu$ gap variation produces larger $\eta$ and results in larger critical thickness.

The above results demonstrate that careful measurements of the transition-temperature variation with thickness could be used to differentiate between the $s$-wave (isotropic) and anisotropic odd- or even-parity superconducting films. The differences between the representative $L=1$ and 2 cases, however, were largely quantitative. It is desirable to find further properties which would help distinguish between $p$- and $d$-wave superconducting films. This distinction is provided by the excitation spectrum in the presence of surface roughness or uniformly distributed impurities. The qualitative results are the same for both kinds of disorder. One can determine the dynamical density of states from Eqs. (3) and (4). The calculation is straightforward but rather lengthy for the surface roughness case when the effective pair-breaking parameter depends on the subband index; the details will be presented elsewhere.[30] For the $p$-wave superconducting film there is a critical strength of a pair-breaking field at which a finite density of states appears at the Fermi surface, while in the $d$-wave case the gaplessness appears even for an infinitesimal amount of diffusive scattering. In the presence of spin-orbit coupling these statements can be generalized, with the exception of a few odd-parity phases which are gapless, to odd- (and predominantly $p$-wave) and even- (and predominantly $d$-wave) parity superconducting films. These results hold even for thicker films ($d > \xi$), as long as no textures appear in the spatial variation of the order parameter.

To summarize, it has been shown here how the variation of the transition temperature with thickness may be used to experimentally determine whether the state of a superconducting film is genuinely anisotropic. The oscillations in $T_c$, which are quite prominent in ordinary superconductors, cannot on general grounds appear in anisotropic ones. Moreover, there is a critical thickness below which the superconductivity vanishes, and this thickness can be quite large for rough surfaces. Furthermore, the temperature variation of various physical quantities is different in odd- and even-parity superconducting films, even-parity superconductors virtually always behaving as gapless. These results are expected to be useful in the ongoing search for a proper diagnostic of exotic superconducting states in heavy-fermion compounds (and possibly in other materials).

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