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Magnetic Field Splitting of the Density of States of Thin Superconductors

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Using Green's-function techniques, we present a theoretical calculation of the behavior of the density of states, free energy, and order parameter of very thin superconductors in a high magnetic field as a function of spin-orbit and spin-flip impurity scattering. In very thin superconducting films without spin scattering, the upper critical field is determined by the Pauli paramagnetism of the normal-metal electrons. Tunneling measurements by Meservey and Tedrow have shown a spin splitting by $2\mu_B H$ in energy space of the BCS peak in the density of states. Zero-temperature calculations of the separate up- and down-spin Green's function for a superconductor show that spin-orbit impurities destroy the magnetic field separation of the peaks in the density of states but do not destroy the energy gap. Spin-flip scattering is much more destructive and destroys both the separation of the peaks and the energy gap. We generalize the calculation to $T \neq 0$ and calculate and plot the critical field versus temperature and the magnetic field dependence of the free energy and order parameter for the various values of the spin-orbit and spin-flip parameter. We also use the theoretical calculations to obtain a fit to the low-temperature tunneling data of Meservey and Tedrow between thin Al and a normal metal and the spin-polarized tunneling between thin Al and ferromagnetic metals.

I. INTRODUCTION

Recently, Tedrow, Meservey, and Schwartz[1] measured the temperature dependence of the critical field of very thin aluminum in a high magnetic field. Pure aluminum was chosen, since previous experiments indicated that spin-orbit scattering was very low and could be neglected in any theoretical analysis. The experiments on very thin Al agreed with the analysis that its critical field was limited by the Pauli paramagnetism. Tedrow and Meservey[2] next performed tunneling experiments between thin Al and a normal metal at low temperature as a function of magnetic field. For zero field, they observed the usual gap in the excitation spectrum with a peak in the density of states at energy (voltage) equal to the gap. However, at a finite value of magnetic field, two peaks in the density of states were observed, one at $\Delta + \mu_B H$ and one at $\Delta - \mu_B H$. As H was increased, the peaks shifted. At first glance, this result is most unusual, since the magnetic field does not act to break the Cooper pairs. However, because of the single-particle nature of the excitation observed by tunneling experiments, one can observe the energy dependence of each spin member of the Cooper pair separately, thus there is a peak at $\Delta + \mu_B H$ and $\Delta - \mu_B H$. It is interesting to note, that the many-body theory developed during the 1960s, for a superconductor in a magnetic field[3] actually had anticipated the experimental results of Tedrow and Meservey, yet none of the theorists suggested doing the experiment. This is due to a few factors which make the experiment difficult. First, one needed a very thin film (< 100 Å) such that the upper critical field was determined by the Pauli paramagnetic condition. Note that magnetic fields ordinarily do not penetrate superconductors so that tunneling in a magnetic field was not seriously considered. Second, spin-orbit scattering has to be small. The structure observed by Tedrow and Meservey would be considerably broadened and unobservable with large spin-orbit scattering. Of the superconducting metals, aluminum is easy to fabricate as a thin film and has a low value of spin-orbit scattering. Third, the two peaks in the density of states can only be observed at temperatures T such that $T/T_c \ll 1$. For thin aluminum, T_c is low ($\simeq 2.5$ K) and so Tedrow and Meservey were forced to work in the more difficult range of He^3 temperatures $\simeq 0.35$ K. Fourth, to get a good separation of the peaks, a large magnetic field on the order of tens of kG was needed. A preliminary explanation of the experiments of Tedrow and Meservey was first presented by Fulde and Engler[4] and by Schwartz[5] who recognized that the density of states could be obtained from the separate Green's function for up- and down-spin superconducting electrons. These Green's functions were discussed by Maki[3] for superconducting electrons in a magnetic field and were later generalized to include magnetic impurities and spin-orbit scattering.[6–8]

The splitting of the superconducting density of states into up- and down-spin states has been used in a very novel way to determine experimentally the polarization of electron spin in ferromagnetic metals. In remarkable experiments by Meservey and Tedrow,[9] high-field tunneling between aluminum and ferromagnetic metals has been used to obtain the relative density of states of majority and minority spin electrons at the Fermi surface of Fe, Co, Ni, and Gd. The theory developed in this paper can be used to get quantitative measures of the polarization of the ferromagnetic metals.

In Sec. II we present the superconducting Green's functions as applied to thin films. In the presence of impurities it is extremely helpful to make use of a 4×4 matrix diagram technique combined with an averaging process developed by Abrikosov and Gorkov[10] and Nambu.[11] In Sec. III we use the spin-up and -down Green's functions to solve for and discuss the density of states. We present detailed numerical calculations of the magnetic field dependence of the density of states of thin-film superconductors with a given value of spin-orbit and spin-flip scattering. Spin-orbit scattering couples the up- and down-spin superconducting electrons and acts to eventually wash out the spin-splitting of the density of states. Spin-flip scattering couples the up- and down-spin superconducting electrons and eventually destroys the energy gap as well as washing out the spin-splitting of the density of states. In Sec. IV we investigate the magnetic field dependence of the order parameter, critical temperature, and the free energy as a function of spin-orbit and spin-flip scattering and magnetic field. In Sec. V we use some of our theoretical results to fit the experimental data of Meservey and Tedrow on thin Al.

II. GREEN'S FUNCTIONS

The most general solutions for the Green's functions of a superconductor with impurity scatterers in a magnetic field have been obtained by Keller and Benda.[12] In their calculation the nonmagnetic scattering centers are described by a potential with a spin-independent $v(\vec{p},\vec{p}\,')$ and spin-orbit v_{so} part:

$$v(\vec{p},\vec{p}\,')+\frac{iv_{so}}{p_F^2}(\vec{p}\times\vec{p}\,')\cdot\vec{\sigma},$$

where $\vec{p}$ and $\vec{p}\,'$ are the momentum of the incoming and scattered electron and p_F is the Fermi momentum. The magnetic (spin-flip) scattering centers are described by a localized moment

$$w_{sf}(\vec{p},\vec{p}\,')\vec{\sigma}\cdot\vec{S}_i,$$

where $\vec{\sigma}$ is the vector spin operator of the electron and $\vec{S}_i$ the vector spin operator of the ith magnetic impurity. The results of the Keller and Benda calculation are

$$\left.\begin{matrix}\mathcal{G}_{\uparrow\uparrow}(\vec{p},\omega_n)\\ \mathcal{G}_{\downarrow\downarrow}(\vec{p},\omega_n)\end{matrix}\right\}=-\frac{i\tilde{\omega}_{n\pm}+\xi}{\tilde{\omega}_{n\pm}^2+\xi^2+\tilde{\Delta}_{n\pm}^2},\qquad \left.\begin{matrix}\mathcal{F}_{\uparrow\downarrow}(\vec{p},\omega_n)\\ \mathcal{F}_{\downarrow\uparrow}(\vec{p},\omega_n)\end{matrix}\right\}=\frac{\pm i\tilde{\Delta}_{n\pm}}{\tilde{\omega}_{n\pm}^2+\xi^2+\tilde{\Delta}_{n\pm}^2}, \tag{1}$$

where $\xi=(p^2/2m)-\mu$ (μ is the chemical potential) and $\tilde{\Delta}_{n\pm}$ and $\tilde{\omega}_{n\pm}$ are the solutions to the following coupled equations:

$$\tilde{\omega}_{n\pm}=\omega_n\pm i\mu_B H+\left(\frac{1}{2\tau}+\frac{1}{2\tau_{so}}+\frac{1}{2\tau_{sf}}\frac{\langle S_z^2\rangle}{S(S+1)}\right)\frac{\tilde{\omega}_{n\pm}}{(\tilde{\omega}_{n\pm}^2+\tilde{\Delta}_{n\pm}^2)^{1/2}}+\frac{T\langle S_z\rangle}{\tau_{sf}S(S+1)}\times\sum_m\left(\frac{1}{\pm i(\omega_n-\omega_m)-\mu_I K}\frac{\tilde{\omega}_{m\mp}}{(\tilde{\omega}_{m\mp}^2+\tilde{\Delta}_{m\mp}^2)^{1/2}}\right)+\frac{1}{\tau_{so}}\frac{\tilde{\omega}_{n\mp}}{(\tilde{\omega}_{n\mp}^2+\tilde{\Delta}_{n\mp}^2)^{1/2}}, \tag{2}$$

$$\tilde{\Delta}_{n\pm}=\Delta+\left(\frac{1}{2\tau}+\frac{1}{2\tau_{so}}-\frac{1}{2\tau_{sf}}\frac{\langle S_z^2\rangle}{S(S+1)}\right)\frac{\tilde{\Delta}_{n\pm}}{(\tilde{\omega}_{n\pm}^2+\tilde{\Delta}_{n\pm}^2)^{1/2}}-\frac{T}{\tau_{sf}}\frac{\langle S_z\rangle}{S(S+1)}\times\sum_m\left(\frac{1}{\pm i(\omega_n-\omega_m)-\mu_I K}\frac{\tilde{\Delta}_{m\mp}}{(\tilde{\omega}_{m\mp}^2+\tilde{\Delta}_{m\mp}^2)^{1/2}}\right)+\frac{1}{\tau_{so}}\frac{\tilde{\Delta}_{n\mp}}{(\tilde{\omega}_{n\mp}^2+\tilde{\Delta}_{n\mp}^2)^{1/2}}, \tag{3}$$

where $\omega_n=(2n+1)\pi T$, T is the temperature, and Δ is the order parameter. The sums over m include only those energies ω_m within the limits of the BCS interaction from $-\omega_D$ to $+\omega_D$. H is the total field acting on the spins of the electrons, applied plus molecular, K is the total field acting on the spins of the impurities, and μ_I is the magnetic moment of a magnetic impurity. τ is the electronic scattering time off the spin-independent potential

$$1/\tau=n_1N(0)\int d\Omega'\,|v(\vec{p},\vec{p}\,')|^2,\quad |\vec{p}\,'|=p_F.$$

τ_{so} is the scattering time off a spin-orbit potential,

$$1/\tau_{so}=\tfrac{1}{3}n_1N(0)\int d\Omega'\,|v_{so}|^2\sin^2\theta.$$

τ_{sf} is the scattering time off a spin-flip impurity

$$1/\tau_{sf}=n_2N(0)S(S+1)\int d\Omega'\,|w_{sf}(\vec{p},\vec{p}\,')|^2,\quad |\vec{p}\,'|=p_F$$

where the $N(0)$ is the electron density of states of one spin direction on the Fermi surface and n_1 and n_2 are the densities of nonmagnetic and magnetic scattering centers. It is assumed that the interaction between the electrons and impurities makes it possible for the field H that acts on the electrons to be different from K, the field that acts on the impurities. Because the impurity spins are coupled to the electron spins, the values of $\langle S_z^2\rangle$ and $\langle S_z\rangle$ are determined largely by the collision frequency with electrons and the size of the field K relative to the value ω_D/μ_B. If $K \gg \omega_D/\mu_B$, the electron interaction cannot flip the spins since they are frozen by the field. In this limit, $\langle S_z\rangle^2 = \langle S_z^2\rangle = S^2$ where S is the impurity spin. If $K \ll \omega_D/\mu_B$ the interaction with the electrons constantly flips the impurity spins so that the impurities do not align and $\langle S_z^2\rangle = \frac{1}{3}S(S+1)$.

Equations (2) and (3) are extremely complex and are solvable only in a few simple limits. The limit of $K \gg \omega_D/\mu_B$ is easy to solve but is not very physical. The equations are

$$\tilde{\omega}_\pm = \omega \pm i\mu_B H + \left(\frac{1}{2\tau} + \frac{1}{2\tau_{so}} + \frac{1}{2\tau_{sf}}\,\frac{S^2}{S(S+1)}\right) \times \frac{\tilde{\omega}_{n\pm}}{(\tilde{\Delta}_{n\pm}^2 + \tilde{\omega}_{n\pm}^2)^{1/2}} + \frac{1}{\tau_{so}}\,\frac{\tilde{\omega}_{n\mp}}{(\tilde{\Delta}_{n\mp}^2 + \tilde{\omega}_{n\mp}^2)^{1/2}}\ , \tag{4}$$

$$\Delta_\pm = \Delta + \left(\frac{1}{2\tau} + \frac{1}{2\tau_{so}} - \frac{1}{2\tau_{sf}}\,\frac{S^2}{S(S+1)}\right) \times \frac{\tilde{\Delta}_{n\pm}}{(\tilde{\Delta}_{n\pm}^2 + \tilde{\omega}_{n\mp}^2)^{1/2}} + \frac{1}{\tau_{so}}\,\frac{\tilde{\Delta}_{n\mp}}{(\tilde{\Delta}_{n\mp}^2 + \tilde{\omega}_{n\mp}^2)^{1/2}}\ . \tag{5}$$

In Eqs. (4) and (5), the sum over the m has vanished so that only the spin-orbit term mixes the spin-up and spin-down states. The spin mixing caused by the magnetic impurities is suppressed by the large field K. The magnetic impurities still act to destroy superconductivity since they act differently on spin-up and spin-down electrons. The depairing parameters is reduced by a factor of $S^2/S(S+1)$ as compared to a situation where there is no magnetic fields and the magnetic impurities are free. This limit of $K \gg \omega_D/\mu_B$ is difficult to achieve in practice. With the molecular field acting on the impurities $K \gg \omega_D/\mu_B$ it is likely that the molecular field caused by the alignment of the impurities acting on the electrons would be greater than Δ/μ_B so that superconductivity could not exist.

The opposite limit of K very small ($K \ll \Delta/\mu_B$) is more physical and more interesting. The zero temperature equations in this limit are

$$\tilde{\omega}_\pm = (\omega \mp \mu_B H) + \left(\frac{1}{2\tau} + \frac{1}{2\tau_{so}} + \frac{1}{6\tau_{sf}}\right)\frac{\tilde{\omega}_\pm}{(\tilde{\Delta}_\pm^2 - \tilde{\omega}_\pm^2)^{1/2}} + \left(\frac{1}{3\tau_{sf}} + \frac{1}{\tau_{so}}\right)\frac{\tilde{\omega}_\mp}{(\tilde{\Delta}_\mp^2 - \tilde{\omega}_\mp^2)^{1/2}}\ , \tag{6}$$

$$\tilde{\Delta}_\pm = \Delta + \left(\frac{1}{2\tau} + \frac{1}{2\tau_{so}} - \frac{1}{6\tau_{sf}}\right)\frac{\tilde{\Delta}_\pm}{(\tilde{\Delta}_\pm^2 - \tilde{\omega}_\pm^2)^{1/2}} + \left(-\frac{1}{3\tau_{sf}} + \frac{1}{\tau_{so}}\right)\frac{\tilde{\Delta}_\mp}{(\tilde{\Delta}_\mp^2 - \tilde{\omega}_\mp^2)^{1/2}}\ . \tag{7}$$

In this limit both magnetic and spin-orbit impurities mix the spin-up and spin-down states. This mixing of spin states produces interesting effects on the density of states as calculated in Sec. III.

III. DENSITY OF STATES

A. Spin-Orbit Scattering

We obtain the density of states of spin-up electrons from the Green's function

$$N_\uparrow(\omega) = \frac{1}{\pi}\int \frac{d^3p}{(2\pi)^3}\,\mathrm{Im}\,\mathcal{G}_{\uparrow\uparrow}(p, -iz)\big|_{z=\omega+i\eta}\ , \tag{8}$$

and similarly for spin-down electrons. The Green's function in the presence of spin-orbit scatterers is given by Eq. (1), where

$$\tilde{\omega}_\pm = \omega \mp \mu_B H + \frac{\tilde{\omega}_\pm}{(\tilde{\Delta}_\pm^2 - \tilde{\omega}_\pm^2)^{1/2}}\left(\frac{1}{2\tau} + \frac{1}{2\tau_{so}}\right) + \frac{\tilde{\omega}_\mp}{(\tilde{\Delta}_\mp^2 - \tilde{\omega}_\mp^2)^{1/2}}\,\frac{1}{\tau_{so}}\ , \tag{9}$$

$$\tilde{\Delta}_\pm = \Delta + \frac{\tilde{\Delta}_\pm}{(\tilde{\Delta}_\pm^2 - \tilde{\omega}_\pm^2)^{1/2}}\left(\frac{1}{2\tau} + \frac{1}{2\tau_{so}}\right) + \frac{\tilde{\Delta}_\mp}{(\tilde{\Delta}_\mp^2 - \tilde{\omega}_\mp^2)^{1/2}}\,\frac{1}{\tau_{so}}\ . \tag{10}$$

The density of states can be expressed simply in terms of the ratio $\tilde{\omega}_\pm/\tilde{\Delta}_\pm = u_\pm$,

$$\left.\begin{matrix} N_\uparrow(\omega) \\ N_\downarrow(\omega) \end{matrix}\right\} = N(0)\,\mathrm{Re}\,\frac{u_\pm}{(u_\pm^2 - 1)^{1/2}}\ . \tag{11}$$

The equations for u_+ and u_- are coupled by the spin-orbit scattering,

$$\frac{\omega \mp \mu_B H}{\Delta} = u_\pm + \frac{1}{\tau_{so}\Delta}\,\frac{u_\pm - u_\mp}{(1 - u_\mp^2)^{1/2}}\ . \tag{12}$$

This equation has been solved in order to find $N_\uparrow(\omega/\Delta)$ and $N_\downarrow(\omega/\Delta)$ as a function of ω/Δ for various values of $1/\tau_{so}\Delta$ and $\mu_B H/\Delta$. The effect of the magnetic field on the calculated curves of $N_\uparrow(\omega/\Delta)$ and $N_\downarrow(\omega/\Delta)$ for a given spin-orbit parameter $1/\tau_{so}\Delta$ is plotted in Figs. 1–3 for a few values of $\mu_B H/\Delta$. Throughout this discussion on the density of states, Δ is the order parameter at a given field, temperature, and impurity concentration. Hence it would be correct to write $\Delta = \Delta(H, T, \tau_{so})$. Though it is often quite difficult to calculate this functional dependence, we sketch some curves for Δ in Sec. IV. The density-of-states curves are quite useful if Δ is treated as a free parameter which can be obtained from a fit of the data to the theory. In all the figures presented we have plotted the density of states above the Fermi surface only. The density of states below the Fermi surface is just the mirror image with the spin assignments reversed. In all

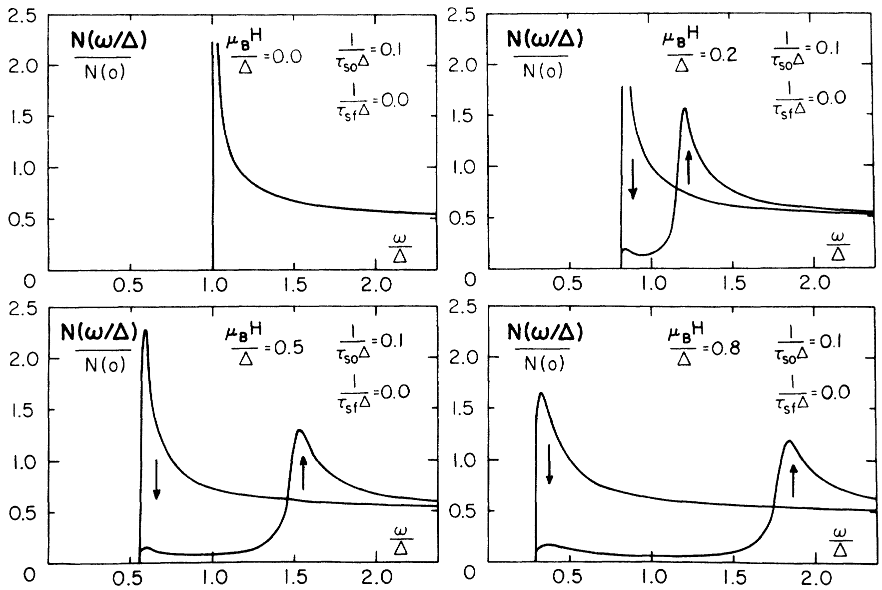

FIG. 1. Density of states for up- and down-spin electrons in a superconductor as a function of magnetic field for a small value of the spin-orbit scattering parameter $1/\tau_{so}\Delta = 0.1$. Note the major effect of the spin-orbit term is to mix the up- and down-spin states with some of the density of states in the peak at $\omega + \mu_B H$ shifted to $\omega - \mu_B H$.

the curves shown, the spin-down density of states is the curve which rises higher and peaks at lower energy. The spin-up density of states peaks at the higher energy. Where the curves are left broken at the top, the peak value is higher than the scale of the axis.

The most obvious feature of these curves is that at zero magnetic field, the presence of spin-orbit scatterers has *no* effect on the density of states. At $\mu_B H/\Delta = 0$, the density of states has just the classic BCS energy behavior. When $\mu_B H/\Delta = 0$, $u_+ = u_- = \omega/\Delta$, so that $N(\omega/\Delta) = N(0)\,\mathrm{Re}\,|\omega/\Delta|/[(\omega/\Delta)^2 - 1]^{1/2}$. However, if we turn on a magnetic field, the density of states does not preserve the simple spin splitting of the BCS curves as with the pure metal or a metal with only regular impurities.

For low values of spin-orbit parameter $1/\tau_{so}\Delta \ll 1$ (Fig. 1) the spin splitting due to the magnetic field is modified slightly. The density of states shows evidence of spin splitting but there are major differences from the density of states of a pure superconducting metal or one with only regular impurities. The infinite peaks in the density of states are rounded off to finite values. The peak of the spin-up density of states, originally at $\Delta + \mu_B H$ gets more severely rounded than that of the spin-down at $\Delta - \mu_B H$. There is a shifting of some of the spin-up density states from the peak at $\Delta + \mu_B H$ to a lower energy at approximately $\Delta - \mu_B H$, leading to another but smaller peak close to where the spin-down curve peaks. As the spin-orbit parameter increases $1/\tau_{so}\Delta \approx 1$ (Fig. 2), the splitting caused by the magnetic field is moderated and the two peaks of the spin-up curve broaden into a single peak. In Fig. 3, where $1/\tau_{so}\Delta \gg 1$, the spin-up and spin-down curve nearly coincide. As the spin-orbit parameter increases, u_+ and u_- become nearly equal so we can make an expansion of the equations in terms of $u = \frac{1}{2}(u_+ + u_-)$ and $v = \frac{1}{2}(u_+ - u_-)$. Adding and subtracting Eq. (12) we get

$$\frac{\omega}{\Delta} = u + \frac{v}{\tau_{so}\Delta}\left(\frac{1}{(1-u_-^2)^{1/2}} - \frac{1}{(1-u_+^2)^{1/2}}\right)$$

$$-\frac{\mu_B H}{\Delta} = v + \frac{v}{\tau_{so}\Delta}\left(\frac{1}{(1-u_-^2)^{1/2}} + \frac{1}{(1-u_+^2)^{1/2}}\right) .$$

Upon expanding in powers of v and neglecting terms of $O(v^2)$ we get

$$\frac{\omega}{\Delta} = u\left(1 - \frac{\frac{1}{2}\tau_{so}\Delta(\mu_B H/\Delta)^2}{(1-u^2)^{1/2}}\right) ,$$

$$v = -\tfrac{1}{2}(\mu_B H/\Delta)\,\tau_{so}\Delta(1-u^2)^{1/2}.$$

As $1/\tau_{so}\Delta$ gets very large, v gets small, and hence $u_\pm \approx u$. u is the solution of the classic depairing equation of Abrikosov and Gorkov[13] with the depairing parameter given by $\frac{1}{2}\tau_{so}\Delta(\mu_B H/\Delta)^2$. The depairing parameter is related to perturbations such as magnetic impurities which act to destroy superconductivity. The larger the depairing parameter, the more superconductivity is destroyed. This depairing manifests itself in the superconducting density of states by rounding off the peak in the density of states and decreasing the energy gap. Notice that this depairing effect is inversely proportional to the spin-orbit parameter so that as $1/\tau_{so}\Delta$ gets much larger than one,

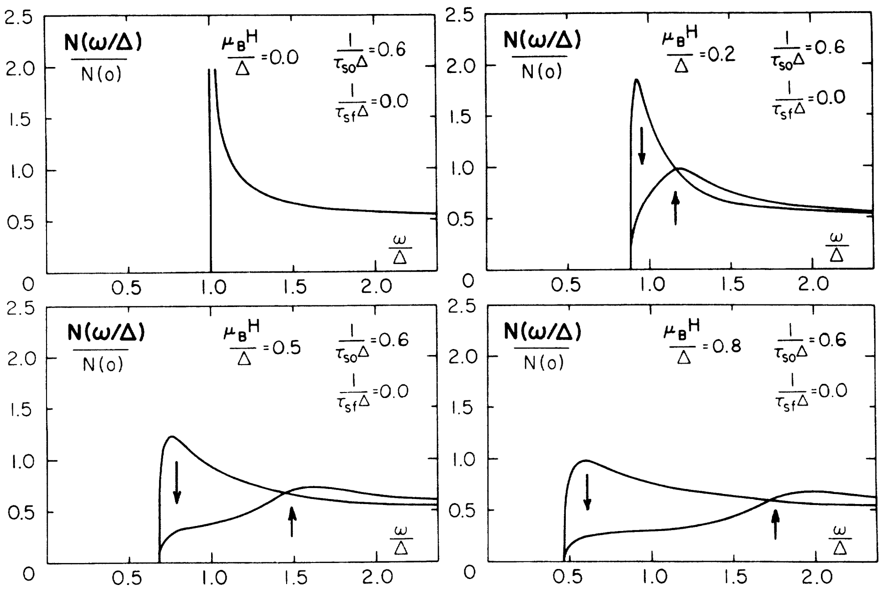

FIG. 2. Density of states with a moderate amount of spin-orbit scattering.

this depairing parameter approaches zero. In this limit, the function v approaches zero and the density of states for both the spin-up and spin-down electrons approaches the simple BCS form with no spin splitting. Figures 1–3 show that the effect of increasing the number of spin-orbit scatterers is to make the spin-up and spin-down density of states more alike, and less split by the magnetic field. At higher values of $1/\tau_{so}\Delta$ the "up" and "down" curves peak nearly at the same energy, and are almost identical.

We can understand the calculated results in Figs. 1–3 from a simple physical point of view by realizing that $N_\uparrow(\omega)[N_\downarrow(\omega)]$ is the number of electrons with up (down) spin at the energy ω. Thus the extra peak of $N_\uparrow(\omega)$ occurs because many spin-down electrons in the peak of $N_\downarrow(\omega)$ get flipped to become a spin-up electron with no change in energy. This also occurs at the large peak of $N_\uparrow(\omega)$ where for low values of spin-orbit parameter, as is seen in Fig. 1, we can detect a slight rise in $N_\downarrow(\omega)$ at $\omega = \Delta + \mu_B H$. In general, spin flips couple the spin-up and spin-down electrons so that $N_\uparrow(\omega)$ and $N_\downarrow(\omega)$ always rise from zero at the same energy value. That is, if $N_\uparrow(\omega)$ is finite, so must $N_\downarrow(\omega)$ be finite. These calculated curves are used to interpret the tunneling data in Sec. V.

The behavior of the superconducting density of

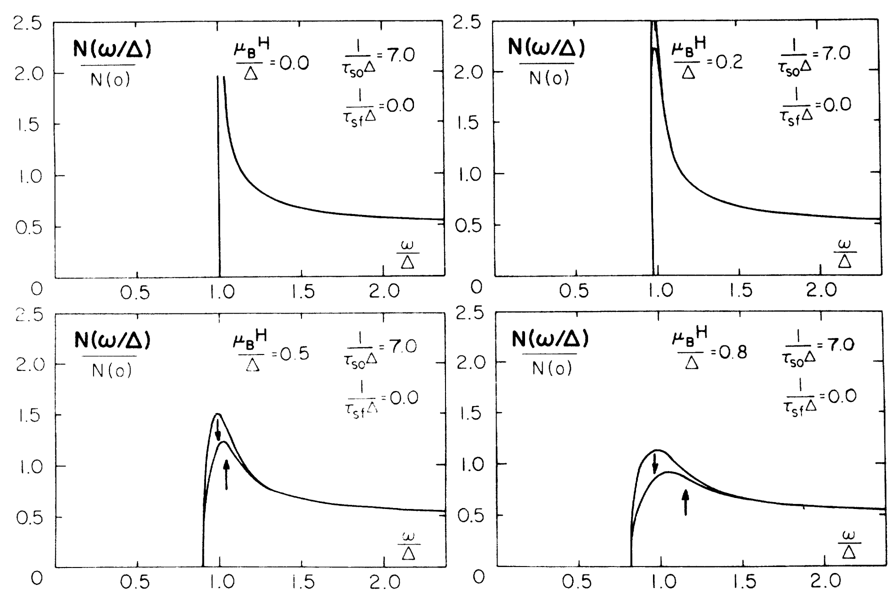

FIG. 3. Density of states with a large amount of spin-orbit scattering.

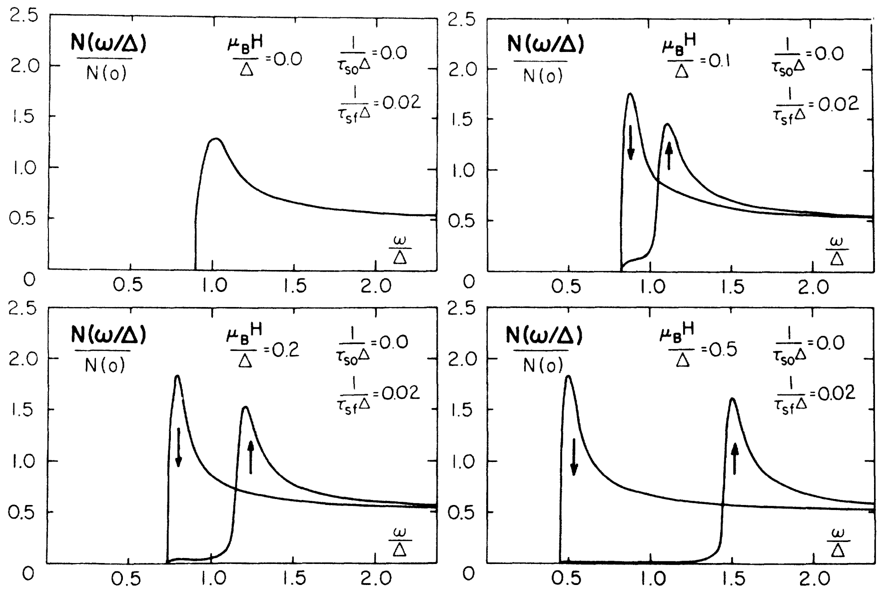

FIG. 4. Density of states for up- and down-spin electrons as a function of magnetic field for a very small value of the spin-flip scattering parameter $1/\tau_{sf}\Delta = 0.02$. In addition to mixing the peaks in the density of states like the spin-orbit impurities do, the spin-flip impurities also act to destroy superconductivity.

states in the presence of spin-orbit scatterers was first described by Fulde and Engler.[14] Recent experiments of Meservey and Tedrow[15] in the tunneling between two thin superconducting Al films supports the details of the theory.

B. Spin-Flip Scattering

In some superconducting metals, impurities with magnetic moments can exist and they have a profound influence on superconductivity. The addition of magnetic impurities sharply decreases the order parameter and can destroy superconductivity at concentrations as low as 1%. This is in marked contrast to spin-orbit or regular impurities which have no effect on the order parameter at zero field. Since both kinds of impurities can flip a spin, we would expect the effects of spin-orbit and magnetic impurities to be similar except that the latter are much more destructive to superconductivity. This is borne out by the calculations which follow.

One new possibility we have to contend with in dealing with magnetic impurities is that the spins can align to create an internal molecular field. Furthermore, the spins can flip in an interaction with an electron so that the dynamics of the spin can be important.

A spin-dynamic calculation has been done by Keller and Benda.[12] In their calculation they have assumed that the electron spins are acted upon by a total field H and the impurity spins by a total field K. In treating the impurity spins dynamically we admit the possibility of inelastic collisions where an electron may have a different energy after it collides with an impurity. By examining Eqs. (2) and (3) one sees that the result of the spin dynamics is to couple the population of electrons at different energies. Unfortunately, this coupling makes the equations much too difficult to solve. However, if the energy exchanged between the impurity and the electron is small compared to energies over which the density of states varies, we can neglect this coupling. This condition is satisfied if $\mu_B K \ll \Delta$, which physically requires the magnetic field acting on the impurity spins to be much less than the energy gap.

For $\mu_B K \ll \Delta$ the density of states are

$$\left.\begin{matrix} N_{\uparrow}(\omega) \\ N_{\downarrow}(\omega) \end{matrix}\right\} = N(0)\,\mathrm{Re}\,\frac{u_{\pm}}{(u_{\pm}^2-1)^{1/2}} ,$$

where $u_{\pm}$ is given by

$$\frac{\omega \mp \mu_B H}{\Delta} = u_{\pm} - \frac{1}{3\tau_{sf}\Delta}\,\frac{u_{\pm}}{(1-u_{\pm}^2)^{1/2}} - \frac{1}{3\tau_{sf}\Delta} \times \left(\frac{u_{\pm}+u_{\mp}}{(1-u_{\mp}^2)^{1/2}}\right) . \quad (13)$$

$1/\tau_{sf}\Delta$ is a measure of the coupling between spin-up and spin-down electrons as well as a depairing parameter.

Spin-flip impurities destroy superconductivity. As $1/\tau_{sf}\Delta$ gets larger, the BCS-like density of states is severely affected and approaches the value of the normal metal. Notice that if $H=0$, $u_+ = u_-$ and the equation for each is

$$\frac{\omega}{\Delta} = u\left(1 - \frac{1}{\tau_{sf}\Delta}\,\frac{1}{(1-u^2)^{1/2}}\right) , \quad (14)$$

which is the Abrikosov-Gorkov depaired equation[13] with a depairing parameter $1/\tau_{sf}\Delta$. Even in the absence of a magnetic field the shape of the density of states is altered as illustrated in the zero-field density-of-states curves in the upper left-hand corner of Figs. 4–6. As $1/\tau_{sf}\Delta$ gets larger, the

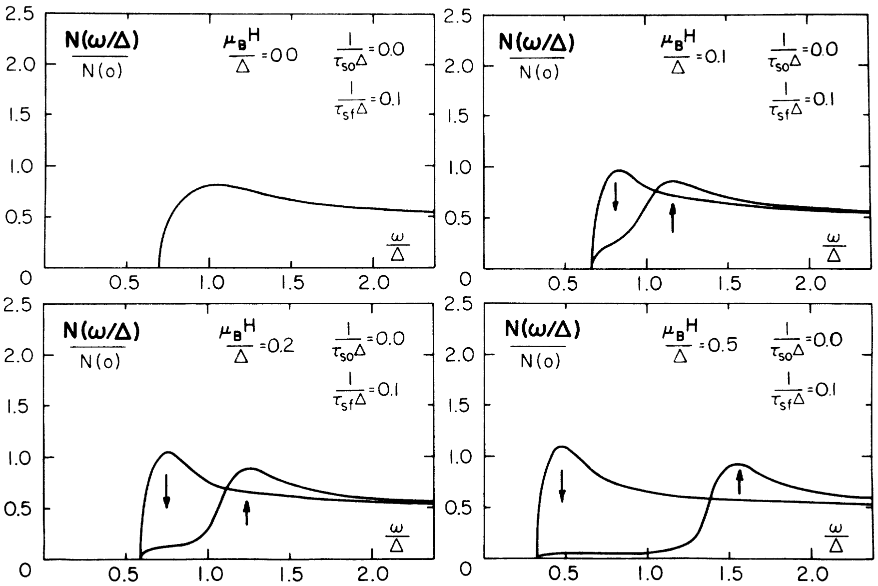

FIG. 5. Density of states with a moderate amount of spin-flip scattering.

BCS peak becomes rounded. When $1/\tau_{sf}\,\Delta \geq 1$, the superconductor becomes gapless; the density of states of the superconductor at the Fermi surface no longer exhibits a gap in energy $[N(\omega=0) \neq 0]$. For $1/\tau_{sf}\,\Delta \gg 1$ the density of states for the superconductor differs very little from that of the normal metal. In the figures, Δ is a function of field, temperature, and concentration of impurities. Magnetic impurities significantly reduce Δ from the pure metal value of Δ_{00} thus increasing significantly the spin-flip parameter $1/\tau_{sf}\,\Delta$ compared with $1/\tau_{sf}\,\Delta_{00}$. In Figs. 4–6 we show the calculation of the field-dependent behavior of the density of states of a superconductor for differing values of $1/\tau_{sf}\,\Delta$. The most striking feature of the field dependence of the density of states with magnetic impurities is that the spin-split peaks are sharper and higher than the unsplit peak. Even at high values of the spin-flip parameter, the peaks of the density-of-states curves increase and become sharper with the application of a magnetic field. As with spin-orbit scatterers, magnetic impurities couple $N_{\uparrow}(\omega/\Delta)$ to $N_{\downarrow}(\omega/\Delta)$ so that the spin-up electrons leak down in energy with $N_{\uparrow}(\omega/\Delta)$ and $N_{\downarrow}(\omega/\Delta)$ becoming now zero at the same value. If $1/\tau_{sf}\,\Delta \gtrsim 1$ the superconductor is nearly gapless. In this regime the application of a magnetic field can cause the superconductor to become gapless

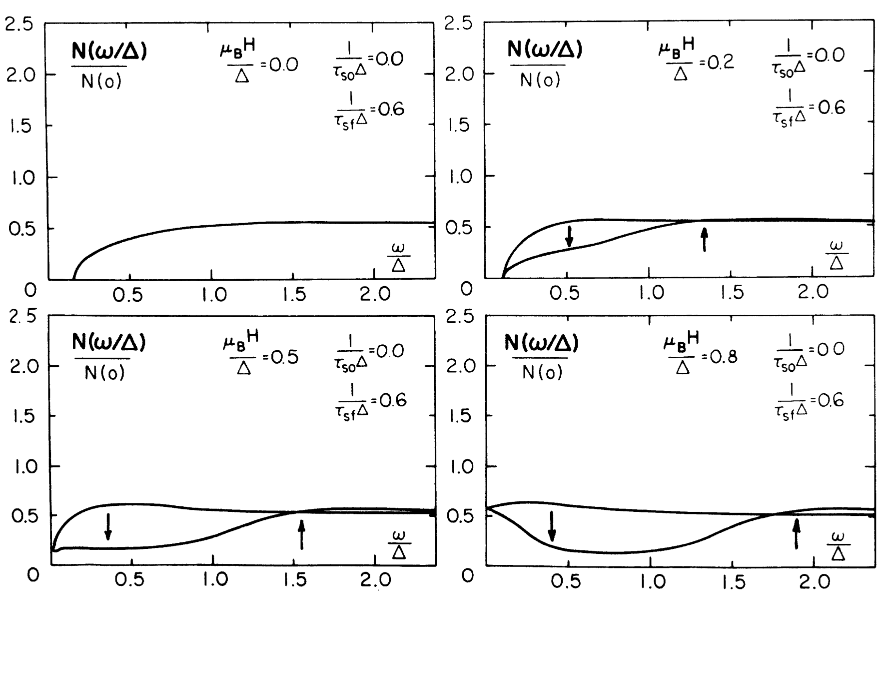

FIG. 6. Density of states with a large amount of spin-flip scattering.

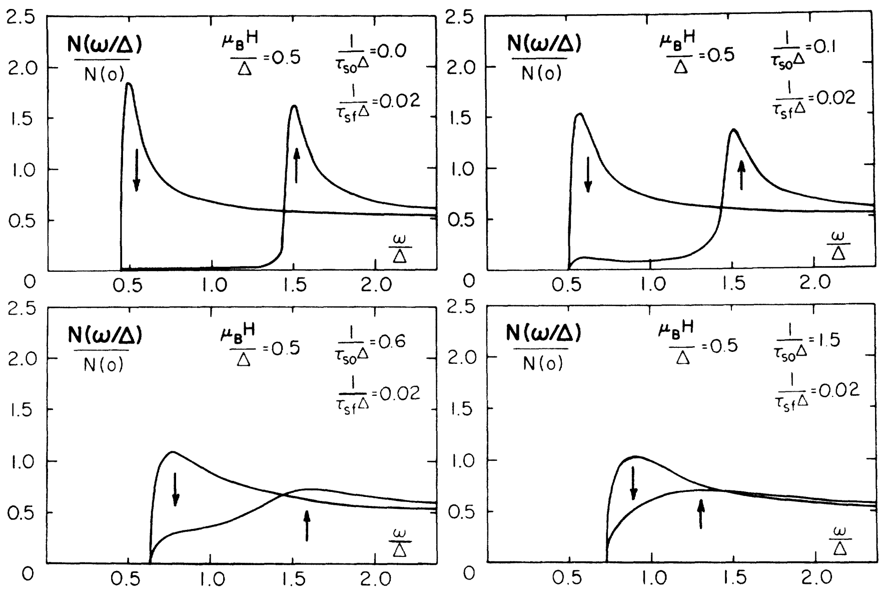

FIG. 7. Effect of spin-orbit scattering on the density of states of a superconductor with constant magnetic field and spin-flip scattering.

as indicated in Fig. 6.

C. Magnetic and Spin-Orbit Impurities Scattering

As a direct generalization of the theory presented in the Sec. III B we find that in the presence of both magnetic and spin-orbit scatterers the density of states is again given by

$$\left.\begin{matrix} N_\uparrow(\omega) \\ N_\downarrow(\omega) \end{matrix}\right\} = N(0)\,\mathrm{Re}\,\frac{u_\pm}{(u_\pm^2-1)^{1/2}}\,,$$

where in this case $u_\pm$ is the solution of the coupled equations

$$\frac{\omega \pm \mu_B H}{\Delta} = u_\pm - \frac{1}{3\tau_{sf}\Delta}\,\frac{u_\pm}{(1-u_\pm^2)^{1/2}} - \frac{1}{3\tau_{sf}\Delta} \times \left(\frac{u_\pm + u_\mp}{(1-u_\mp^2)^{1/2}}\right) + \frac{1}{\tau_{so}\Delta}\left(\frac{u_\pm - u_\mp}{(1-u_\mp^2)^{1/2}}\right) . \quad (15)$$

We have solved these equations numerically, and we show the density-of-states curves obtained in Figs. 7 and 8. In Fig. 7 we hold the spin-flip parameter $1/\tau_{sf}\,\Delta$ constant and vary the spin-orbit parameter $1/\tau_{so}\,\Delta$. Increasing the spin-orbit parameter from 0 to $\gg 1.0$ gradually changes the density-of-states curve of a given $1/\tau_{sf}\,\Delta$ and $\mu_B H/\Delta$ to the density of curve for the same $1/\tau_{sf}\,\Delta$ with the effects of the magnetic field suppressed. This is seen analytically if we write down the equations for $u_\mp$ in the high spin-orbit limit. The result is

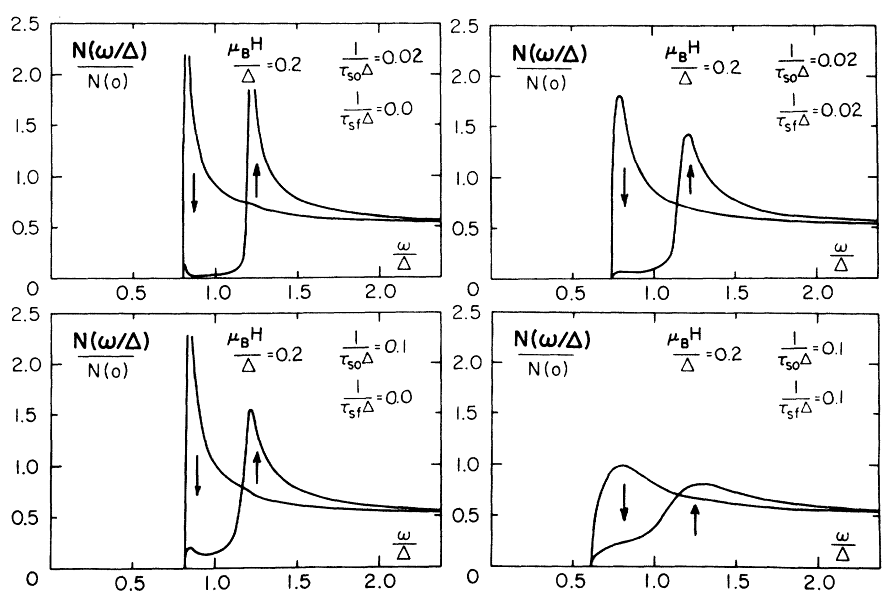

FIG. 8. Effect of spin-flip scattering on the density of states of a superconductor with constant magnetic field and two values of spin-orbit scattering.

$$\omega/\Delta = u(1 - 1/\tau_{sf}\Delta)[1/(1-u^2)^{1/2}],$$

where $u_\pm \approx u$. This is identical to Eq. (14) for only magnetic impurities at zero magnetic field.

At zero magnetic field, a superconductor with magnetic impurities as an energy gap as long as $1/\tau_{sf}\Delta < 1$. It can appear gapless in a magnetic field because of the shift in the density of states caused by the magnetic field. Since increasing the spin-orbit scattering reduces the effect of a magnetic field, the gap can reappear. However, if $1/\tau_{sf}\Delta \geq 1$, the system is always gapless and we cannot induce an energy gap no matter how large we choose $1/\tau_{so}\Delta$.

In Fig. 8 we illustrate the effect of adding magnetic impurities to a superconductor at a fixed value of $1/\tau_{so}\Delta$ and $\mu_B H/\Delta$. As $1/\tau_{sf}\Delta$ increases, the peaks in the density of states become more rounded and the energy gap decreases. As $1/\tau_{sf}\Delta \to 1$ the peaks are very poorly defined. For $1/\tau_{sf}\Delta > 1$ the peaks are even more broadened and the energy gap is zero. In general, magnetic impurities are destructive to superconductivity. The calculations show that the spin-flip parameter exerts a stronger influence than the spin-orbit parameter on the density of states.

IV. THERMODYNAMICS OF THIN-FILM SUPERCONDUCTORS

A. Order Parameter

As a measure of the strength of superconductivity, the order parameter is very important. In terms of the finite temperature Green's function:

$$\Delta = \frac{-|g|}{2} iT \sum_{|\omega_n|<\omega_D} \int \frac{d^3p}{(2\pi)^3} \times (\mathfrak{F}^+_{\uparrow\downarrow}(p,\omega) - \mathfrak{F}^+_{\downarrow\uparrow}(p,\omega)). \quad (16)$$

The $\mathfrak{F}^+$ functions for a thin film in a magnetic field are given by Eq. (1) and yield for the order parameter

$$\Delta = |g| T \sum_{|\omega_n|<\omega_D} \int \frac{d^3p}{(2\pi)^3} \mathrm{Re}\left(\frac{\tilde{\Delta}_{n+}}{\tilde{\omega}^2_{n+} + \xi^2 + \tilde{\Delta}^2_{n+}}\right). \quad (17)$$

The momentum integral is performed using contour integration giving

$$\Delta = |g| N(0)\, 2\pi T \sum_{0<\omega_n<\omega_D} \mathrm{Re}\,\frac{1}{(1+u_n^2)^{1/2}}. \quad (18)$$

We solve this equation approximately for small Δ by expanding $u_{n\pm}$ in powers of Δ and grouping all the terms of a given power of Δ together. For all but the lowest-order coefficient we take the sum over ω_n out to infinity without adding a significant contribution. However, the lowest-order term does not converge so we use a standard calculational device which enables us to sum to infinity. The result is

$$-\ln\frac{T}{T_{c0}} = \sum_{n\geq 0} \mathrm{Re}\left(\frac{2\pi T}{u^{(0)}_{n+}} - \frac{2\pi T}{\omega_n}\right) + \left(\frac{\Delta}{2\pi T}\right)^2 \times \sum_{n\geq 0} \frac{1}{2}\mathrm{Re}\left[\left(\frac{2\pi T}{u^{(0)}_{n+}}\right)^2 (1 + 2u^{(0)}_{n+} u^{(1)}_{n+})\right], \quad (19)$$

where

$$u_{n+} = (1/\Delta)(u^{(0)}_{n+} + u^{(1)}_{n+}\Delta^2 + u^{(2)}_{n+}\Delta^4 + \cdots).$$

The supercooling critical field as a function of temperature is obtained from Eq. (19) by setting $\Delta = 0$. It can also be used to solve for Δ in the limit of $\Delta/2\pi T$ as a small parameter.

An exact equation for Δ may be obtained from Eq. (18) if we convert the sum over ω_n to a contour integral using a function which has a simple pole at every ω_n. The result of this lengthy but standard calculation is

$$\ln\frac{\Delta}{\Delta_{00}} = \int_0^\infty d\left(\frac{\omega}{\Delta}\right)\left[\tfrac{1}{2}\,\mathrm{Im}\left(\frac{1}{(1-u_+^2)^{1/2}} + \frac{1}{(1-u_-^2)^{1/2}}\right) \times \tanh\frac{\beta\omega}{2} - \mathrm{Im}\,\frac{1}{[1-(\omega/\Delta)^2]^{1/2}}\right], \quad (20)$$

where $u_\pm$ refer to the zero-temperature Green's function. This equation however is extremely difficult to solve numerically and an analytic solution cannot be found.

B. Free Energy

The free energy may be found from an analytical expression for the order parameter using the very general thermodynamic equation:

$$G_s - G_n = \int_0^\Delta \Delta^2 d(1/|g|). \quad (21)$$

A general analytic solution of Δ as a function of $1/|g|$ could not be obtained so that the free energy cannot be calculated exactly in all regimes. In the limit of small $\Delta/2\pi T$ however, one can use Eq. (19) to find the free energy. Since

$$T_{c0} = (2\omega_D\gamma/\pi)e^{-1/N(0)|g|},$$

upon differentiation of Eq. (19) with respect to $1/|g|$ we obtain

$$d\left(\frac{1}{|g|}\right) = -N(0)\left(2C_2\frac{\Delta}{(2\pi T)^2} + 4C_4\frac{\Delta^3}{(2\pi T)^4} + \cdots\right)d\Delta, \quad (22)$$

where C_2 and C_4 are the coefficients of $\Delta/2\pi T$ and $(\Delta/2\pi T)^2$ in Eq. (19). Maki and Tseuento[3] and Maki[6] pointed out that $C_2 = 0$ determines the critical point at which the superconducting to normal-state transition changes its order. If C_2 is negative, the transition is first order. If C_2 is positive, the transition is second order. Using Eqs. (21) and (22) we calculate $G_s - G_n$:

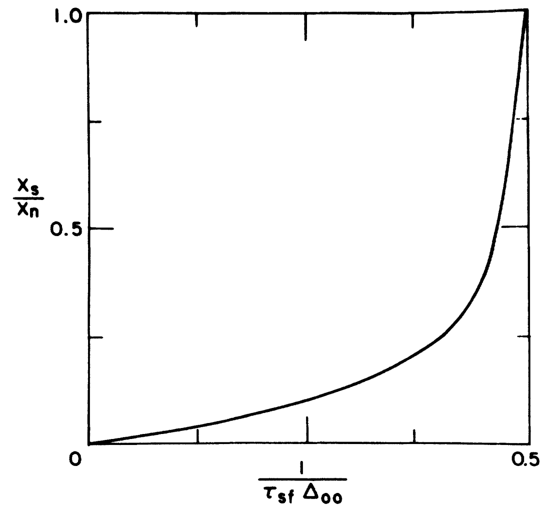

FIG. 9. Spin susceptibility of a superconductor as a function of spin-flip scattering.

$$G_s - G_n = -N(0)\left(\frac{C_2}{2}\,\frac{\Delta^4}{(2\pi T)^2} + \frac{2C_4}{3}\,\frac{\Delta^6}{(2\pi T)^4} + \cdots\right). \tag{23}$$

Since this expression is valid only for small $\Delta/2\pi T$, we must resort to approximate methods close to $T=0$. We will also need to know the dependence of the superconducting free energy on the magnetic field. To obtain this free-energy dependence exactly is very difficult. However, at low fields, we may approximate the field-dependent free-energy difference by

$$G_s(H) - G_n(0) = -\tfrac{1}{2}N(0)\,\Delta_{00}^2 - \tfrac{1}{2}\chi_s H^2, \tag{24}$$

where χ_s is the susceptibility of the superconducting state at zero magnetic field with either spin-orbit or spin-flip scatterers. Normally for a superconductor at $T=0$, $\chi_s/\chi_n=0$. However, both spin-orbit and spin-flip scatterers destroy spin as a good quantum number and tend to increase the value of χ_s/χ_n. The superconducting-state susceptibility has been calculated in the presence of either spin-orbit or spin-flip impurities by Maki and Fulde[16]:

$$\frac{\chi_s}{\chi_n} = 1 - 2\pi T \sum_{n\geq 0}^{\infty}\left\{1\Big/(1+u_n^2)\,\Delta\left[(1+u_n^2)^{1/2} - \frac{1}{3\tau_{sf}\Delta}\right.\right.$$
$$\left.\left.\times\left(\frac{2u_n^2+1}{u_n^2+1}\right)\frac{2}{\tau_{so}\Delta}\right]\right\}, \tag{25}$$

where u_n is given by

$$\frac{\omega_n}{\Delta} = u_n\left(1 - \frac{1}{\tau_{sf}\Delta}\,\frac{1}{(1+u_n^2)^{1/2}}\right)$$

and

$$\omega_n = 2\pi T(n+\tfrac{1}{2}).$$

This function is numerically calculated for magnetic impurities and is presented in Fig. 9. Using this low-field approximation of the superconducting free energy together with the calculations of the supercooling field and change of order, we can present a very good plot of the behavior of $G_s(H) - G_n(0)$ for all values of magnetic field.

C. Very Thin Film with Spin-Orbit Impurities

1. Supercooling Curves ($\Delta = 0$)

Using Eq. (19) we substitute the u_{n+} expansion for spin-orbit impurities and we arrive at the following expression for the supercooling critical field versus temperature:

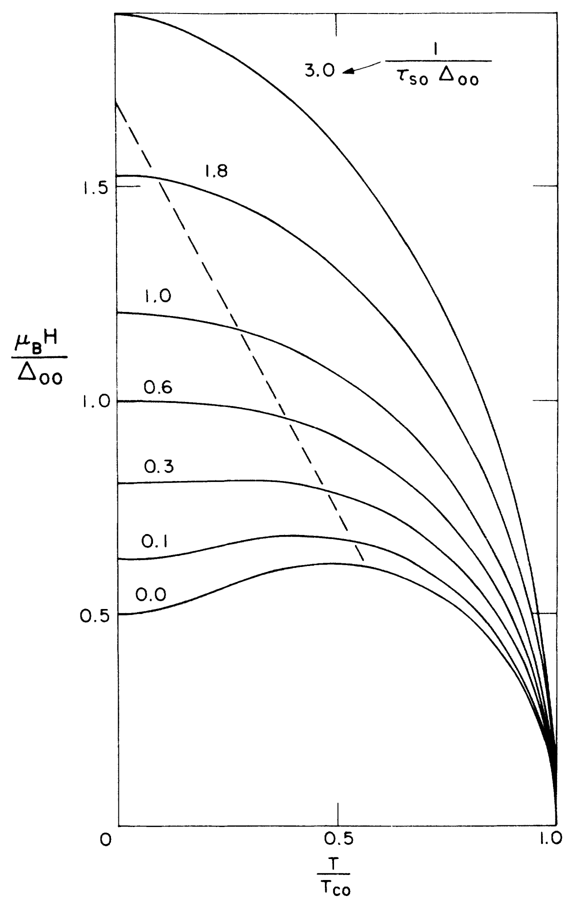

FIG. 10. Critical-field–vs–temperature curve of the second-order phase transition for a paramagnetically limited superconductor. For values of $1/\tau_{so}\Delta > 2.32$. The order of transition is always second order. For $1/\tau_{so}\Delta < 2.32$ the intersection of the dashed line with the solid lines gives the temperature below which the transition is first order.

$$\ln(t) = \sum_{n=0}^{\infty} \mathrm{Re}\left(\frac{2\pi T}{u_{n+}^{(0)}} - \frac{1}{n+\frac{1}{2}}\right) , \tag{26}$$

where

$$\frac{u_{n+}^{(0)}}{2\pi T} = (n+\tfrac{1}{2}) + i\alpha \frac{\mu_B H}{\Delta_{00}}\left(\frac{1}{2\gamma t}\right),$$

$$\alpha = \left[(n+\tfrac{1}{2}) - \frac{i\mu_B H}{\Delta_{00}}\left(\frac{1}{2\gamma t}\right)\right] \Big/ \left[(n+\tfrac{1}{2}) + \frac{2}{\tau_{so}\Delta_{00}} \times\left(\frac{1}{2\gamma t}\right) - i\frac{\mu_B H}{\Delta_{00}}\left(\frac{1}{2\gamma t}\right)\right] , \tag{27}$$

$$t = \frac{T}{T_{c0}}, \quad \gamma = 1.7811.$$

In Fig. 10, the critical field $\mu_B H/\Delta_{00}$ is plotted versus the reduced temperature t for various values of the spin-orbit parameter $1/\tau_{so}\Delta_{00}$. Observe the difference between the Δ-normalized parameters of Sec. III, $1/\tau_{so}\Delta$, $\mu_B H/\Delta$, and these parameters $1/\tau_{so}\Delta_{00}$, $\mu_B H/\Delta_{00}$ normalized to Δ_{00}. The relationship between Δ and Δ_{00} can be obtained from the dependence of the order parameter on H and τ_{so}. Δ_{00} we must remember, is the order parameter at zero field, temperature and impurity concentration. We have also calculated C_2 of Eq. (23) so that we may find the effect of spin-orbit impurities on the critical point at which the order of the phase transition changes:

$$C_2 = \tfrac{1}{2}\,\mathrm{Re}\left\{\sum_n \left[\left(\frac{2\pi T}{u_{n+}^{(0)}}\right)^3 (1 + 2u_{n+}^{(0)}u_{n+}^{(1)})\right]\right\} , \tag{28}$$

where $u_{n+}^{(0)}$ is given by Eq. (27) and

$$u_{n+}^{(1)} = \left\{\frac{0.5}{\tau_{so}\Delta_{00}2\gamma t}\;\frac{u_{n+}^{(0)} - u_{n-}^{(0)}}{u_{n-}^{(0)}} \Big/ \left[1 + \frac{1}{\tau_{so}\Delta_{00}2\gamma t}\left(\frac{1}{u_{n+}^{(0)}} + \frac{1}{u_{n-}^{(0)}}\right)\right]\right\}\left[\left(\frac{1}{u_{n-}^{(0)}}\right)^2 + \frac{1}{\tau_{so}\Delta_{00}2\gamma t}\;\frac{1}{u_{n+}^{(0)}u_{n-}^{(0)}}\left(\frac{1}{u_{n-}^{(0)}} - \frac{1}{u_{n+}^{(0)}}\right)\right] \tag{29}$$

$$u_{n-}^{(0)} = (u_{n+}^{(0)})^*.$$

The locus of critical points as we increase $1/\tau_{so}\Delta_{00}$ is shown by the dotted line in Fig. 10. Notice that the addition of spin-orbit scatterers raises the supercooling field and at the same time drives the first-order transition to a higher field and lower temperature. At $1/\tau_{so}\Delta_{00} = 2.32$, the transition is second order even at $T = 0$. This agrees with the results reported earlier by Fulde.[17] At this concentration of spin-orbit scatterers the ($T = 0$) superheating, supercooling, and regular critical field converge. For $1/\tau_{so}\Delta_{00} \geq 2.32$, the transition is always second order and there is no superheating or supercooling field. We can understand this rise in critical fields in a qualitative way by realizing that a superconductor with spin-orbit impurities has a spin susceptibility unequal to zero, which means superconducting electrons can respond to an applied magnetic field much like normal metals. The critical field obtained from equating the free energies is much larger than the Pauli paramagnetic field H_p which is obtained when the superconducting electrons do not respond to the field.

2. *Order Parameter ($T = 0$)*

The exact equation for the order parameter is too difficult to solve. Nevertheless, by using approximate methods we can sketch the dependence of the order parameter upon the magnetic field and spin-orbit impurities. The curves $\Delta(H)/\Delta_{00}$ are shown in Fig. 11 for various values of $1/\tau_{so}\Delta_{00}$. Notice that the combined effect of a magnetic field and spin-orbit impurities is to decrease the order parameter. For small H, $\Delta(H)$ descends quadratically with H. This is because $1/\tau_{so}\Delta_{00}$ and $\mu_B H/\Delta_{00}$ together create a depairing effect proportional to H^2. As $1/\tau_{so}\Delta_{00}$ is increased to 2.32, the quadratic dependence of $\Delta(H)$ increases and reaches a maximum at $1/\tau_{so}\Delta_{00} = 2.32$. Below $1/\tau_{so}\Delta_{00} = 2.32$, the $\Delta(H)$ curves are double valued with $d\Delta(H)/dH = \infty$ corresponding to the superheating critical field and [$\Delta(H) = 0$] corresponding to the supercooling critical field. Above $1/\tau_{so}\Delta_{00} = 2.32$, the $\Delta(H)$ curves are single valued. As we increase

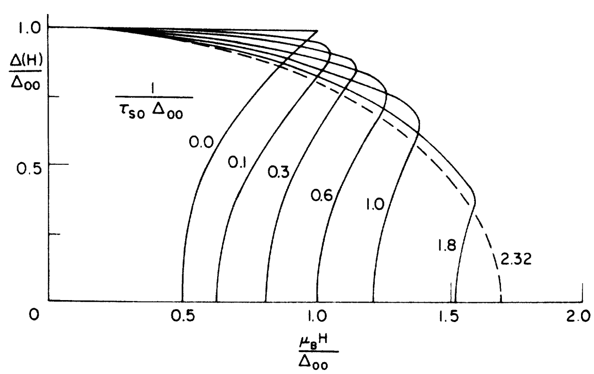

FIG. 11. Sketch of the field dependence of the order parameter as a function of spin-orbit scattering. For $1/\tau_{so}\Delta < 2.32$ the order parameter is double valued due to the first-order nature of the transition giving rise to a superheating and supercooling transition as well as the thermodynamic transition.

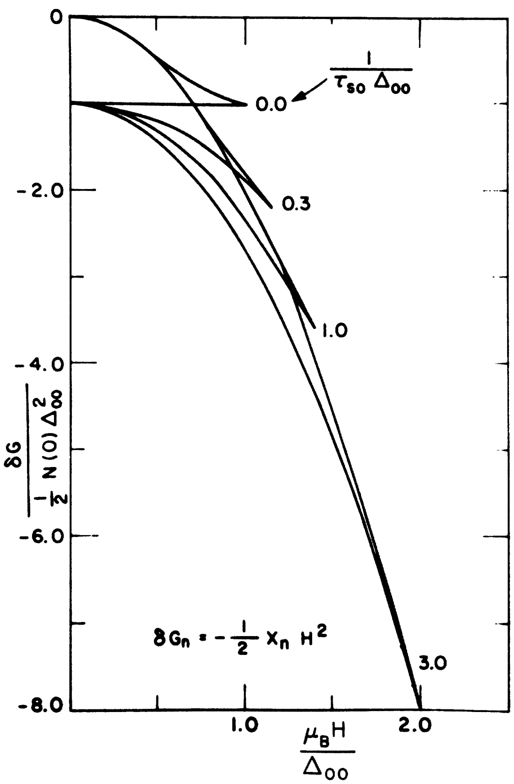

FIG. 12. Sketch of the field dependence of the free energy of the superconductor and normal metal as a function of spin-orbit scattering. For spin-orbit parameter $1/\tau_{so}\Delta < 2.32$ the transition is first-order indicated by the crossing of the superconducting free energy with the parabolic normal-state paramagnetic-susceptibility energy $-\frac{1}{2}\chi_n H^2$.

$1/\tau_{so}\Delta_{00}$ from 2.32, the depairing effect becomes smaller so that the $\Delta(H)$ curves become less steep. Note that as we vary the spin-orbit parameter the $\Delta(H)$ curves continuously deform into each other. The curves for $1/\tau_{so}\Delta_{00} < 2.32$ all cross the dotted curve of $\Delta(H)$ for $1/\tau_{so}\Delta_{00} = 2.32$. Above $1/\tau_{so}\Delta_{00} = 2.32$, the order of the transition is always second order so the $\Delta(H)$-vs-H curve is single valued.

3. *Free Energy (T = 0)*

With the supercooling critical field exactly known and the superheating field determined by Fig. 11, the magnetic field dependence of the superconducting free energy can be quite well determined without an exact calculation. We approximate the low-field dependence by using the zero-field susceptibility given by Eq. (25). This susceptibility is identical to the result of Abrikosov and Gorkov.[18] As a function of $1/\tau_{so}\Delta_{00}$, χ_s rises from zero and approaches 1 asymptotically as $1/\tau_{so}\Delta_{00}$ gets large. We expect that Eq. (24) will be a good approximation to the free energy for small H. Since the spin-orbit impurities do not appreciably affect the normal state, the normal-state free energy is

$$\delta G_n = G_n(H) - G_n(0) = -\tfrac{1}{2}\chi_n H^2 . \qquad (30)$$

At high-field values, the superconducting susceptibility χ_s has a magnetic field dependence $\chi_s(H)$. When $1/\tau_{so}\Delta_{00} \geq 2.32$ the susceptibility has a sufficient field dependence that the free energy of the normal and superconducting states intersect tangently. This susceptibility increases as H increases because the depairing parameter gets larger. The depairing parameter is proportional to H^2. At low fields we expect this effect to be very small so that our low-field approximation is expected to hold quite well. In Fig. 12 we have plotted the superconducting and normal-state free energies as a function of $\mu_B H/\Delta_{00}$ for selected values of the spin-orbit parameter $1/\tau_{so}\Delta_{00}$. For low values of $1/\tau_{so}\Delta_{00}$, where the transition is first order, the supercooling and superheating extremum are connected by an unphysical free-energy curve. For $1/\tau_{so}\Delta_{00} \geq 2.32$, the order of the transition changes and the superconducting and normal free energies merge at a single-field value, which is the second-order transition field. Note, for example, the $1/\tau_{so}\Delta_{00} = 3.0$ curve. The intersection of G_n and G_s occurs at $\mu_B H/\Delta_{00} = 1.9$. If the susceptibility with spin-orbit impurities $\chi_s(H)$ did not increase from the zero-field value of 0.8, the two curves would intersect at a lower-field value of $\mu_B H/\Delta_{00} = 1.59$. This is expected since the low-field approximation where the H dependence of χ_s can be neglected is only valid in the limit $\mu_B H/\Delta_{00} < 1$.

This completes our discussion of the thermodynamics of very thin films with spin-orbit impurities. It is possible to extend this discussion to finite temperature, but the effect of temperature is to round off and disguise the effects we are most interested in.

D. Thin Film with Magnetic Impurities

We present the thermodynamics of the thin film with magnetic impurities. The similarities to the spin-orbit case are many, but there are also some significant differences.

1. *Supercooling Critical-Field Curves (Δ = 0)*

As with spin-orbit impurities, we expand u_{n+} in powers of Δ and obtain the following expression for the supercooling critical-field versus temperature and magnetic impurity parameter $1/\tau_{so}\Delta_{00}$:

$$\ln t = \sum_{n=0}^{\infty} \left[\mathrm{Re}\left(\frac{2\pi T}{u_{n+}^{(0)}} - \frac{1}{n+\frac{1}{2}} \right) \right] ,$$

where

$$\frac{u_{n+}^{(0)}}{2\pi T} = (n+\tfrac{1}{2}) + \frac{1}{\tau_{st}\Delta_{00}}\left(\frac{1}{2\gamma t}\right) + \alpha\,\frac{i\mu_B H}{\Delta_{00}}\left(\frac{1}{2\gamma t}\right)$$

and

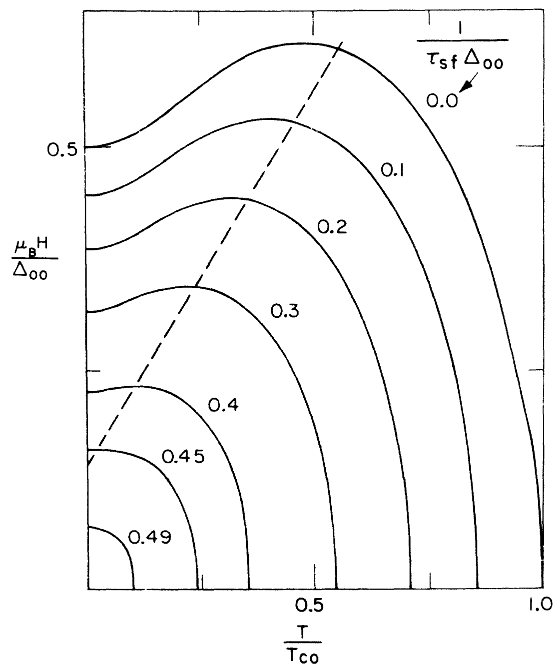

FIG. 13. Critical-field–vs–temperature curve of the second-order phase transition for a paramagnetically limited superconductor. For values of $1/\tau_{sf}\Delta > 0.461$, the order of the transition is always second order. For $1/\tau_{sf}\Delta < 0.461$ the intersection of the dashed line with the solid lines give the temperature below which the transition is first order.

$$\alpha = \left[n + \frac{1}{2} - \frac{i\mu_B H}{\Delta_{00}}\left(\frac{1}{2\gamma t}\right) + \frac{1}{\tau_{sf}\Delta_{00}}\left(\frac{1}{2\gamma t}\right)\right] \times \left[n + \frac{1}{2} - \frac{i\mu_B H}{\Delta_{00}}\left(\frac{1}{2\gamma t}\right) + \frac{1}{3\tau_{sf}\Delta_{00}}\left(\frac{1}{2\gamma t}\right)\right]^{-1}. \tag{31}$$

In Fig. 13 this critical field $\mu_B H/\Delta_{00}$ is plotted versus the reduced temperature t for a number of values of spin-flip impurity parameter $1/\tau_{sf}\Delta_{00}$. Notice that unlike spin-orbit impurities, the presence of magnetic impurities lowers the critical-field values. Even though the magnetic impurities give the superconductor a susceptibility which would tend to raise the critical field, the destructive effect of the magnetic impurities more than offsets the rise so that the total effect is that the critical field declines. We have calculated the coefficient of the $(\Delta/2\pi T)^2$ term. The change in sign of this coefficient determines the order of the superconducting to normal transition:

$$C_2 = \tfrac{1}{2}\,\mathrm{Re}\left\{\sum_n \left[\left(\frac{2\pi T}{u_{n+}^{(0)}}\right)\left(1 + 2u_{n+}^{(0)}u_{n+}^{(1)}\right)\right]\right\},$$

where $u_{n+}^{(0)}$ is defined above and

$$u_{n+}^{(1)} = -\tfrac{1}{2}b\left[\left(1 - \frac{b}{u_{n+}^{(0)}}\right)Z - \frac{b u_{n+}^{(0)}}{u_{n-}^{(0)2}}Z^*\right]\Big/\left(1 - \frac{b}{u_{n+}^{(0)}} - \frac{b}{u_{n-}^{(0)}}\right),$$

$$Z = \left(\frac{1}{u_{n+}^{(0)}}\right)^2 + \frac{u_{n+}^{(0)} + u_{n-}^{(0)}}{[u_{n-}^{(0)}]^3}, \tag{32}$$

$$u_{n-}^{(0)} = (u_{n+}^{(0)})^*, \quad b = \frac{1}{3\tau_{sf}\Delta_{00}}\left(\frac{1}{2\gamma t}\right).$$

This coefficient has been calculated and the locus of points at which it assumes a value of zero is indicated by the dashed line in Fig. 13. For temperatures to the right of the dashed line the transition is second order and therefore the critical-field curve plotted is the actual critical field. To the left of the dashed line, the transition is first order and the transition plotted in Fig. 13 is the supercooling curve.

Note that unlike spin-orbit impurities, the net effect of magnetic impurities is to decrease the zero-field critical temperature. Increasing $1/\tau_{sf}\Delta_{00}$ also drives the critical point at which the order of the transition changes to a lower field and temperature. For $1/\tau_{sf}\Delta_{00} > 0.461$ the superconducting-normal transition is second order at all temperatures. As shown in Fig. 14, the density of states of the superconductor is gapless at zero field when $1/\tau_{sf}\Delta_{00} \geq 0.456$. Thus, to destroy the first-order transition in a magnetic field requires a concentration of magnetic impurities slightly greater than the concentration at which the superconductor becomes gapless. At this concentration where $1/\tau_{sf}\Delta_{00} = 0.461$, the supercooling, superheating, and actual critical fields merge.

2. *Order Parameter*

To discuss the magnetic field dependence of the order parameter, we first describe the well-known

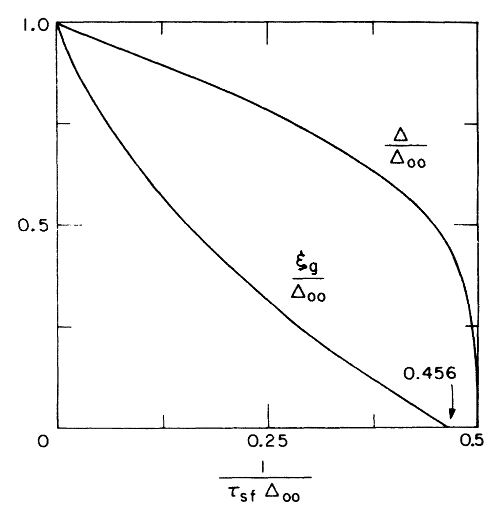

FIG. 14. Dependence of the order parameter Δ and energy gap ξ_g on the amount of spin-flip scattering.

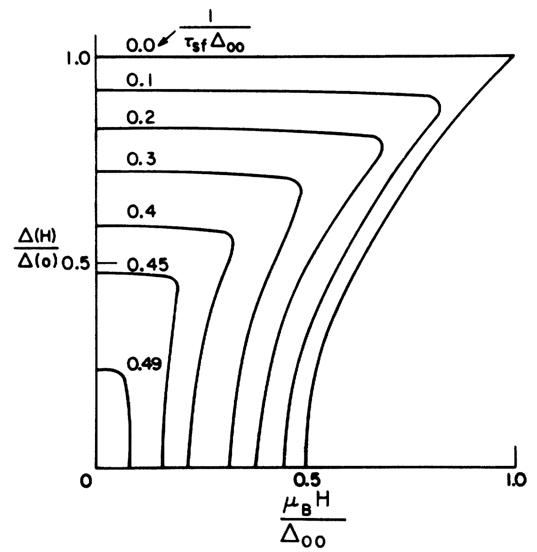

FIG. 15. Sketch of the field dependence of the order parameter as a function of spin-flip scattering. For $1/\tau_{sf}\Delta<0.461$ the order parameter is double valued.

dependence of the order parameter on $1/\tau_{sf}\,\Delta_{00}$ at zero field. This is plotted in Fig. 14 along with the magnetic impurity–dependent energy gap ξ_g. Notice that above $1/\tau_{sf}\,\Delta_{00}=0.456$, $\xi_g=0$, and a severe decline in the order parameter occurs. The gaplessness caused by a magnetic field through spin splitting of the density of states also causes a severe decline in the order parameter. At $1/\tau_{sf}\,\Delta_{00}=0.5$ the order parameter is zero and superconductivity is completely destroyed.

In Fig. 15, we have sketched the curves of $\Delta(H)/\Delta_{00}$ at various values of $1/\tau_{sf}\,\Delta_{00}$. At zero field, the order parameter is simply that of a superconductor with magnetic impurities and has the value given in Fig. 14. As the magnetic field is increased, the order parameter decreases quadratically with $\mu_B H/\Delta_{00}$ with a very small coefficient. The coefficient is calculated and plotted in the Appendix. As the magnetic field is increased further, the superconductor eventually becomes gapless with a sharp decrease in the order parameter. The sharp decrease in the order parameter in Fig. 15 occurs at a value of $\mu_B H/\Delta_{00}$ approximately equal to the energy gap ξ_g/Δ_{00} in Fig. 14 for the same concentration of impurities. For $1/\tau_{sf}\,\Delta_{00}<0.461$, the $\Delta(H)$ curves are double valued, their extreme points corresponding to the supercooling and superheating fields.

3. Free Energy (T = 0)

In analogy with the discussion of spin-orbit impurities, we use the zero-field susceptibility of Eq. (25) to approximate the free energy at low-field values. This susceptibility is shown in Fig. 9.

Note that χ_s/χ_n remains relatively small until $1/\tau_{sf}\,\Delta_{00}$ approaches its gapless value of 0.456 when it rapidly increases to one at $1/\tau_{sf}\,\Delta_{00}=0.5$. Gaplessness greatly increases the spin susceptibility of the superconducting state since the electrons of the broken pairs can align themselves with the field. Unlike spin-orbit impurities, magnetic impurities destroy superconductivity and considerably increase the zero-field free energy. An expression for this energy is given by Maki,[19]

$$\begin{aligned} G_s(0)-G_n(0) &= -\tfrac{1}{2}N(0)\Delta^2(1-\tfrac{1}{2}\pi\xi+\tfrac{2}{3}\xi^2) \quad \text{if} \quad \xi\le 1 \\ &= -\tfrac{1}{2}N(0)\Delta^2[1-\xi\sin^{-1}(1/\xi) \\ &\quad +\xi^2[1-(1-\xi^2)^{1/2}]-\tfrac{1}{2}\xi^2 \\ &\quad \times\{1-[1-(1/\xi^2)]^{3/2}\}], \quad \text{if} \quad \xi>1 \end{aligned} \tag{33}$$

where

$$\xi = 1/\tau_{sf}\,\Delta.$$

Using this expression for the zero-field energy difference together with the low-field approximation, we obtain a very good description of the impurity and magnetic field dependence of the free-energy difference. The free energy versus field energy for selected values of the magnetic impurity parameter is shown in Fig. 16. Because the susceptibility is quite low for all but the highest value of $1/\tau_{sf}\,\Delta_{00}$, we note that the $G_s(H)$ curves are very flat in the low-field region. As the magnetic field increases, the spin splitting of the density of states gets larger so that the superconductor approaches gaplessness.

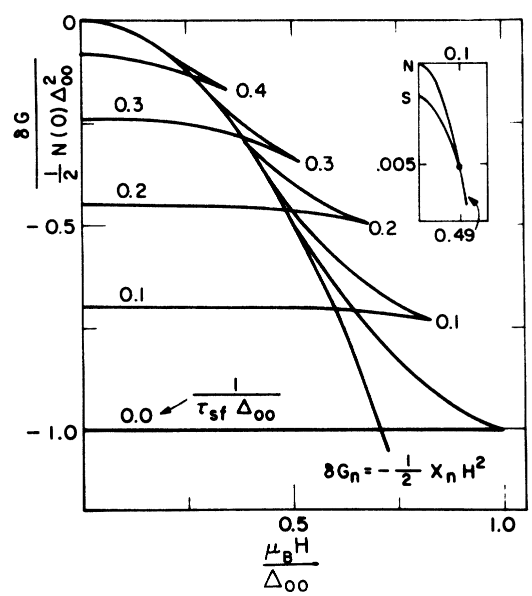

FIG. 16. Sketch of the field dependence of the free energy of the superconductor and normal metal as a function of spin-flip scattering. For spin-flip parameter $1/\tau_{sf}\Delta<0.491$ the transition is first order.

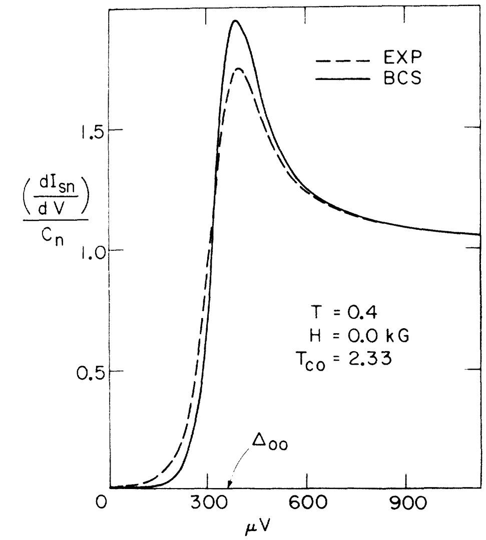

FIG. 17. Fit of the density of states from the BCS theory with the measured density of states of a thin Al film.

The susceptibility rapidly increases when the field is close to ξ_g/μ_B, where ξ_B is the zero-field energy gap shown in Fig. 14. Therefore, as the magnetic field approaches ξ_g/μ_B, the free energy of the superconducting state decreases rapidly. When $1/\tau_{sf}\,\Delta_{00} \geq 0.461$, the zero-field susceptibility is already greater than $0.75\chi_n$ so that the enhanced susceptibility is sufficiently large to ensure that the normal and superconducting curves intersect each other tangently.

The free-energy and order-parameter curves sketched in this section give a very physical picture for discussing the detailed behavior of very thin films in a high magnetic field.

V. COMPARISON OF THEORY WITH EXPERIMENTAL DATA

The dashed line in Fig. 17 is a tracing of the x-y recording of the conductance versus voltage at zero magnetic field obtained in an experiment by Meservey and Tedrow at $T = 0.4$ K for a thin Al film with $T_c = 2.33$ K. The theoretical conductance for a BCS superconductor with an energy gap related to T_c by the relation $2\Delta_{00} = 3.52\ k_B T_c$ is shown by the solid line. Except for the increased broadening of the experimental curve, the theoretical curve is a reasonable fit. The reason for this broadening is not known but is probably related to the difference between a very thin film and an ideal BCS superconductor. The broadening cannot be attributed to magnetic impurities since metallic Al does not allow for the formation of a magnetic moment about an impurity. The broadening in the field-free film sets a limit on the quality of the fit one can expect to obtain for films in a magnetic field.

The convolution of the theoretical superconducting density of states with a temperature function

$$\frac{\beta}{(e^{\beta(\omega+eV)/2}+e^{-\beta(\omega+eV)/2})^2} = F(\omega+eV) \tag{34}$$

shifts the voltage of the conductance maximum higher than the zero-temperature peak of the density of states obtained from setting $eV = \Delta_{00}$.

The dashed line in Fig. 18 is the experimental conductance for the same Al film but with a magnetic field of 22.44 kG applied parallel to the film. The 22.44-kG magnetic field yields a value of 0.369 for the parameter $\mu H/\Delta_{00}$. The solid line in Fig. 18 is the theoretical fit obtained from the field-dependent calculation of the density of states for a BCS superconductor without spin-orbit scatterers. The expression for the conductance is

$$I_{sn} = C_n \int_{-\infty}^{+\infty} d\omega\, \tfrac{1}{2}\, \mathrm{Re}\left(\frac{|\omega-\mu_B H|}{[(\omega-\mu_B H)^2-\Delta^2]^{1/2}} + \frac{|\omega+\mu_B H|}{[(\omega+\mu_B H)^2-\Delta^2]^{1/2}}\right) F(\omega+eV). \tag{35}$$

The amount of spin splitting in the data agrees with the calculated value of

$2\mu_B H/\Delta_{00} = 0.369$.

A better fit to the experimental data is obtained by recognizing that spin-orbit scattering acts to transport spin-up electrons from the high peak to the low peak. The dotted line is a theoretical curve obtained by calculating the superconducting density of states with a spin-orbit parameter $1/\tau_{so}\Delta_{00} = 0.06$. The calculation presented in Fig. 11 [Sec. IV] shows that the order parameter $\Delta(H)$ is essentially unchanged from its zero-field value of Δ_{00}. This value for the spin-orbit parameter yields a con-

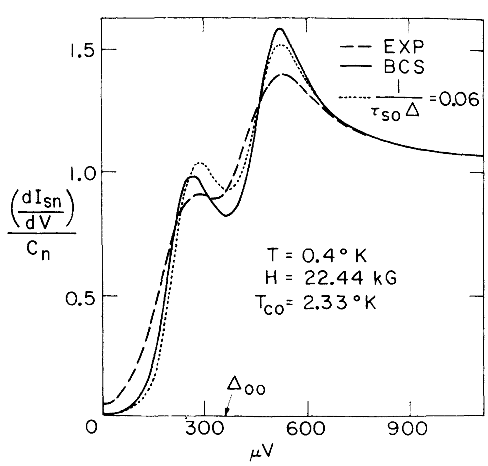

FIG. 18. Fit to the density of states of a thin Al film in a magnetic field including the effects of spin-orbit scattering.

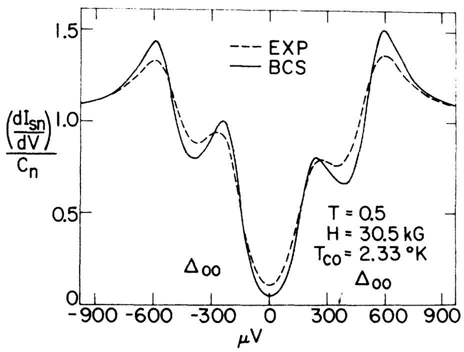

FIG. 19. Fit to the density of states between thin Al film and ferromagnetic Ni. The fit is made with polarization of Ni of 0.08.

ductance curve which gives a better fit to the low-voltage and high-voltage peak and also locates the peaks somewhat better than the simple spin-split BCS density of states. Another effect of spin-orbit impurities is a slight increase in the energy gap in a magnetic field.

The dashed line of Fig. 19 shows the experimental conductance for the tunneling from superconducting Al into a ferromagnet, i.e., Ni. Note that unlike tunneling into a nonferromagnetic normal metal, the conductance is nonsymmetric in voltage. Since each peak in the spin-split density of states is associated with a separate spin, tunneling can be used to obtain the relative density of states of up- and down-spin electrons at the Fermi surface of the ferromagnetic Ni. Assuming the tunneling process does not flip the spin of the tunneling electron, the relative heights of the spin-split peaks are related to $N_\uparrow(0)$ and $N_\downarrow(0)$ for Ni. In paramagnetic metals $N_\uparrow(0)=N_\downarrow(0)$, but in ferromagnetic metals $N_\uparrow(0)$ need not equal $N_\downarrow(0)$. The theoretical expression which can be used to fit the experimental data is

$$\frac{dI_{sf}}{dV}=C_n\int_{-\infty}^{+\infty}d\omega\left(\frac{N_{\mathrm{Ni}\uparrow}(0)N_\uparrow(\omega)}{N_{\mathrm{Ni}}(0)N(0)}+\frac{N_{\mathrm{Ni}\downarrow}(0)N_\downarrow(\omega)}{N_{\mathrm{Ni}}(0)N(0)}\right)F(\omega+eV), \tag{36}$$

where $N_{\mathrm{Ni}}(0)=N_{\mathrm{Ni}\uparrow}(0)+N_{\mathrm{Ni}\downarrow}(0)$, $N_\uparrow(\omega)$ and $N_\downarrow(\omega)$ are the density of states for aluminum in the superconducting state, and $N(0)$ is the density of states of aluminum in the normal state. If we define a polarization P as

$$P=[N_{\mathrm{Ni}\uparrow}(0)-N_{\mathrm{Ni}\downarrow}(0)]/N_{\mathrm{Ni}}(0),$$

the tunneling current can be rewritten

$$\frac{dI_{sf}}{dV}=C_n\int_{-\infty}^{+\infty}d\omega\left[\left(\frac{1+P}{2}\right)\frac{N_\uparrow(\omega)}{N_1(0)}+\left(\frac{1-P}{2}\right)\times\frac{N_\downarrow(\omega)}{N_1(0)}\right]F(\omega+eV). \tag{37}$$

The solid line in Fig. 19 is a theoretical fit of a spin-split density of states with a value for the polarization $P=0.11$. This tunneling technique from a superconductor into a ferromagnet developed by Meservey and Tedrow[9] has been used to directly measure the polarization of Co, Fe, and Gd as well as Ni.

The polarization values obtained by Meservey and Tedrow are not in agreement with the simple band picture for ferromagnetic metals. Similar anomalous results have been obtained by Bush *et al.*[20,21] analyzing the spin spectra of electrons excited by photoemission from ferromagnetic metals. The experiments differ in that the polarizations of Meservey and Tedrow are associated with electrons within millivolts of the Fermi surface whereas the photoemission technique probes electrons much deeper in the electron bands. These anomalous polarization values have stimulated a great deal of theoretical analysis. The spin splitting of the density of states of superconductors has been developed into a very powerful technique to determine the relative spin polarization in magnetic metals as well as to determine superconducting metal parameters.

Thus far, tunneling experiments in high magnetic fields have been performed only on thin Al films where the spin-orbit effects are small. To get a more quantitative fit one should include the depairing effect of the orbital term. Further experiments are presently being carried out on other metals with larger values of the spin-orbit parameter. Our curves will be useful in interpreting these experiments. As yet, experimentalists have not considered the problem of tunneling into thin films with magnetic impurities. Our calculations predict spectacular changes in the density of states and energy gap as a function of spin-flip parameter and magnetic field. The theoretical calculations for spin-flip impurities have assumed that the impurity spin is relatively free to flip. One expects that in the experimental sample, the molecular fields will modify the scattering effects of the magnetic impurities. In such cases a more general expression of the spin-dependent impurity Green's function will have to be used in the calculations.

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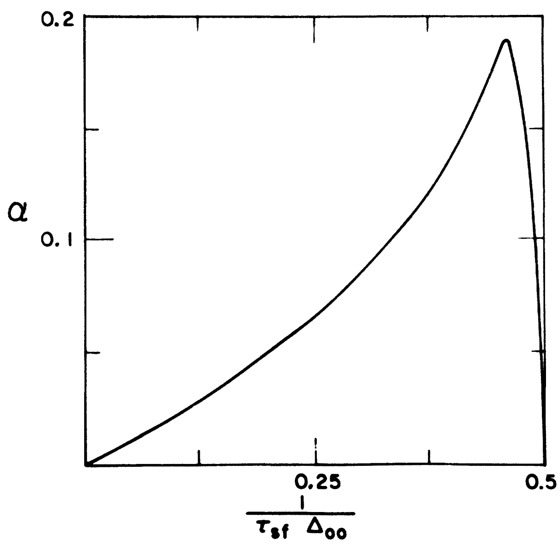

FIG. 20. Plot of α as a function of spin-flip scattering.

APPENDIX: THIN-FILM ORDER PARAMETER WITH MAGNETIC IMPURITIES

We investigate rigorously the low-field behavior of the order parameter of a thin film with magnetic impurities. We start with an expression which is a slight variation of Eq. (20)

$$\ln\frac{\Delta}{\Delta_{00}}=\frac{\pi T}{\Delta}\sum_{n\geq 0}^{\infty}\left(\frac{1}{(1+u_{n+}^2)^{1/2}}+\frac{1}{(1+u_{n-}^2)^{1/2}}\right)-\int_{-\infty}^{\infty}\frac{d(\omega/\Delta)}{[1+(\omega/\Delta)^2]^{1/2}}\ . \quad \text{(A1)}$$

Expanding u_{n+} in powers of $\mu_B H/\Delta$, where Δ equals the order parameter at zero field:

$$u_{n+}=u_{0n}+x_{1n}(\mu_B H/\Delta)+x_{2n}(\mu_B H/\Delta)^2,$$

$$u_{n-}=u_{0n}+s_{1n}(\mu_B H/\Delta)+s_{2n}(\mu_B H/\Delta)^2,$$

where

$$\frac{\omega_n}{\Delta}=u_{0n}\left(1-\frac{1}{\tau_{sf}\Delta}\frac{1}{(1+u_{0n}^2)^{1/2}}\right),$$

$$x_{1n}=s_{1n}^{*}=i\left[1-\frac{1}{3\tau_{sf}\Delta}\left(\frac{1+2u_{0n}^2}{(1+u_{0n}^2)^{3/2}}\right)\right], \quad \text{(A2)}$$

$$x_{2n}=s_{2n}=-\frac{1}{2}\frac{x_{1n}^2u_{0n}}{3\tau_{sf}\Delta}\frac{5-4u_{0n}^2}{(1+u_{0n}^2)^{5/2}}\times\left(1-\frac{1}{\tau_{sf}\Delta(1+u_{0n}^2)^{1/2}}\right)^{-1}.$$

At $T=0$, Eq. (A1) is written

$$\ln\frac{\Delta}{\Delta_{00}}=\int_0^{\infty}d\left(\frac{\omega}{\Delta}\right)\frac{1}{2}\left(\frac{1}{(1+u_+^2)^{1/2}}+\frac{1}{(1+u_-^2)^{1/2}}\right)-\int_0^{\infty}\frac{d(\omega/\Delta)}{[1+(\omega/\Delta)^2]^{1/2}}, \quad \text{(A3)}$$

where u_+ and u_- become continuous variables. Expanding Eq. (A3) in powers of $\mu H/\Delta$ we find that the linear term is zero. The second-order term is

$$C\left(\frac{\mu_B H}{\Delta}\right)^2=C\left(\frac{\mu_B H}{\Delta_{00}}\right)^2\left(\frac{\Delta_{00}}{\Delta}\right)^2,$$

where

$$C=\int_0^{\infty}\frac{d(\omega/\Delta)}{(1+u_0^2)^{3/2}}\left(-u_0x_2-\tfrac{1}{2}x_1^2\frac{1-2u_0^2}{1+u_0^2}\right). \quad \text{(A4)}$$

Taking the derivative of Eq. (A3) with respect to $\mu_B H/\Delta_{00}$,

$$\frac{d^2}{d(\mu_B H/\Delta_{00})^2}\ln\frac{\Delta}{\Delta_{00}}\bigg|_{H=0}=\frac{\Delta_{00}}{\Delta(0)}\frac{d^2(\Delta/\Delta_{00})}{d(\mu_B H/\Delta_{00})^2}\bigg|_{H=0}=2C\left(\frac{\Delta_{00}}{\Delta(0)}\right)^2,$$

shows that the expansion of $\Delta(H)/\Delta_{00}$ in powers of $\mu_B H/\Delta_{00}$ is related to C by

$$\frac{\Delta(H)}{\Delta_{00}}=\frac{\Delta(0)}{\Delta_{00}}+C\frac{\Delta_{00}}{\Delta(0)}\left(\frac{\mu_B H}{\Delta_{00}}\right)^2.$$

The coefficient C has been evaluated numerically and is negative. We define $\alpha=-C\Delta_{00}/\Delta(0)$ to obtain

$$\frac{\Delta(H)}{\Delta_{00}}=\frac{\Delta(0)}{\Delta_{00}}-\alpha\left(\frac{\mu_B H}{\Delta_{00}}\right)^2. \quad \text{(A5)}$$

The plot of α as a function of $1/\tau_{sf}\Delta_{00}$ is shown in Fig. 20. For small values of $1/\tau_{sf}\Delta_{00}$ the decrease in the order parameter is very slight. The largest values of α is obtained for values of $1/\tau_{sf}\Delta_{00}$ slightly greater than the gapless regime.

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