gy one could easily obtain the absorption linewidths.

Returning to Eq. (4), the sum over $\vec{q}$ is evaluated by transforming to an integral. Thus one finds

$$\sum_{\vec{q}} |g(\vec{q})|^2 = 2\sqrt{2}\,\pi\alpha\left(\frac{\mu_B H}{\hbar\omega_l}\right)^{1/2}(\hbar\omega_l)^2. \qquad (5)$$

The closest approach of the levels occurs when $E(n=0)+\hbar\omega_l = E(n=1)$. Then

$$\mathcal{E}_+ - \mathcal{E}_- = 2\Big[\sum_{\vec{q}} |g(q)|^2\Big]^{1/2} = 2\sqrt{2}\left(\frac{2\pi\mu_B H}{\hbar\omega_l}\right)^{1/4}\alpha^{1/2}\hbar\omega_l. \qquad (6)$$

From the data of Ref. (1) this splitting is about 1 meV. Eq. (6) then implies that $\alpha = 0.02$.

In order to compare our results with the infrared absorption, $h\nu$, we must recognize that the transition originates on the $n=3$ heavy-hole valence level. The energy of this level is given by Eq. (1) with a minus sign in front of the square-root term and the appropriate effective mass. Since the experiment of Ref. 1 was performed at about 30°K, the parameters quoted below Eq. (1) for liquid-helium temperatures must be modified. The only parameter which changes appreciably in going from 4.2 to 30°K is the gap, $E_g$. For InSb this decreases with increasing temperature by approximately $2\times10^{-4}$ eV/deg.[4] Using the value $E_g \approx 226$ meV, we have plotted the predicted infrared absorption frequency as a function of magnetic field in Fig. 3. The data of Ref. (1) are indicated by the open circles. Considering that this is a "first-principles" calculation, the agreement is quite good. Small adjustments of $E_g$, $m^*(0)$, and $g^*(0)$, within their experimental error, will lead to even better agreement. Notice that our Eq. (4) predicts that the upper and lower branches of the $|n=0; 1_{\vec{q}}\rangle$ level asymptotically approach the same line, whereas Fig. 3 of Ref. 1 implies that they approach different lines. We feel that the experimental data do not extend far enough out the $|n=0; 1_{\vec{q}}\rangle$ level to warrant the drawing of such straight lines.

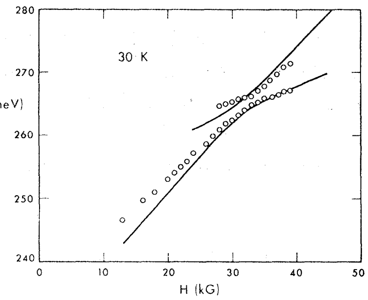


FIG. 3. Field dependence of the infrared absorption in InSb. The solid lines are the theoretical results of Eq. (4). The open circles are the data of Ref. 1.

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## ANOMALOUS DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE ON PARAMAGNETIC IMPURITIES*

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It is shown that magnetic ordering of paramagnetic impurities in superconducting alloys gives rise to a very different dependence of the superconducting transition temperature on the concentration of paramagnetic impurities than is expected for paramagnetic alloys.[1] In particular, it is explained when the superconducting transition temperature will decrease more rapidly than one expects for paramagnetic alloys. Also an explanation is given for the anomalous slow decrease and increase in the superconducting transition temperature occurring for increasing concentration of paramagnetic impurities over a small range of impurity concentrations just below the critical concentration of paramagnetic impurities which destroys superconductivity. Since such an anomalous behavior of the superconducting transition temperature results if the spins of the paramagnetic impurities are ordered and not free to rotate, the behavior of the superconducting transition temperature at high concentrations of paramagnetic impurities might be used as a further diagnostic tool for studying the problem of coexistence of superconductivity and magnetism.

If the impurity spins are not free to rotate but fixed by a field which might vary from impurity to impurity, and which results from the coupling among the paramagnetic impurities, then conduction-electron scattering by the paramagnetic impurities involving spin flips is inelastic and reduced. Neglecting for the moment other effects resulting from impurity spin ordering, the result is that the superconducting transition temperature should be higher than it would be if the impurity spins were free to rotate.[2] The rapid decrease in the superconducting transition temperature following the anomalous slow decrease and increase in the transition temperature arises from (a) the electronic spin polarization at the Fermi surface, resulting from the magnetization of the paramagnetic impurities each having a spin $S$, and (b) from the electronic scattering which is proportional to $cS(S+1)$, which increases more rapidly with increasing impurity concentration $c$ than the spin-flip scattering decreases. Clearly, if the electronic spin polarization at the Fermi surface, which tends to suppress superconductivity, is more effective than the reduction of the spin-flip scattering, then the superconducting transition temperature will decrease more rapidly with increasing impurity concentration as it would be for paramagnetic alloys. It is shown that spin-orbit scattering plays an important role in the interplay of Fermi surface gliding and reduction of electronic spin-flip scattering.

The anomalous dependence of the superconducting transition temperature on the concentration of paramagnetic impurities has been observed in lanthanum alloys containing small concentrations of gadolinium impurities.[3,4] The reduction of the electronic scattering involving spin flips and occurring if the impurity spins become ordered should also give rise to an anomalous behavior of other properties as, for example, the density of states,[5] electronic specific heat,[6] thermal conductivity, energy gap, nuclear relaxation time, etc.

It is well known that even small concentrations of paramagnetic impurities have a drastic effect on the properties of superconductors. Since the superconducting transition temperature is related to the spin but not to the magnetic moment of the paramagnetic impurities, it is assumed that the strong effects of the paramagnetic impurities on the superconducting properties arise from an $s$-$d$ exchange interaction between the conduction electrons and the paramagnetic impurities involving spin-flip electron scattering which has obviously a strong destructive effect on Cooper pairs. If the system of paramagnetic impurities is in the paramagnetic state, then only negligibly small crystalline fields due to crystal anisotropy act on the otherwise freely rotating impurity spins. The conduction electrons are then mainly elastically scattered by the paramagnetic impurities. The effect of the paramagnetic impurities on the superconducting transition temperature is then determined by the electronic collision time resulting from the $s$-$d$ exchange interaction. This collision time is proportional to $cS(S+1)$. Neglecting in the theory real and inelastic electronic scattering, and also the anomalous $s$-$d$ scattering first treated by Kondo,[7,8] theory and experiment agree reasonably well in determining the superconducting transition temperature $T_c$ up to paramagnetic impurity concentrations close to the critical concentration which destroys superconductivity.[4] Typically for dilute alloys containing paramagnetic impurities, for example $La_{1-x}Gd_x$, the superconducting transition temperature $T_c$ at such impurity concentrations becomes of the same order as the temperature for which magnetic ordering of the impurity spins occurs. The dependence of the superconducting transition temperature on the paramagnetic impurities is approximately determined by the electronic collision time $\tau_{ex}'$ resulting from the $s$-$d$ exchange interaction, which is proportional to

$$c[S(S+1)-S\langle B_S(\beta\omega_z)\tanh(\tfrac{1}{2}\beta\omega_z)\rangle_{av}],$$

where $B_S$ denotes the Brillouin function, $\beta=(kT)^{-1}$, $T$ denotes the temperature, $\omega_z$ is the impurity-spin Zeeman energy, and the average $\langle\,\rangle_{av}$ is performed over the distribution of Zeeman energies. The term which is subtracted from $S(S+1)$ results from electronic spin-flip scattering involving $\langle S_-S_+\rangle$ and $\langle S_+S_-\rangle$, where $S_-$ and $S_+$ denote the usual spin-wave creation and annihilation operator, respectively. Obviously, the reduction of the $s$-$d$ exchange scattering results only in the presence of fields fixing the impurity spins. Apparently fixing the impurity spins by a field has the same effect as reducing the impurity concentration to an effective concentration

$$c_{\text{eff}} = c\left[1 - \frac{\langle B_S(\beta\omega_z)\tanh(\tfrac{1}{2}\beta\omega_z)\rangle_{\text{av}}}{S+1}\right].$$

It therefore takes a higher impurity concentration to obtain the same transition temperature, relative to the case when free rotation of the impurity spins is assumed (neglecting for the moment the change in the transition temperature arising from the electronic spin polarization at the Fermi surface).

A more rigorous treatment of the electronic scattering due to the paramagnetic impurities taking into account fixing of the impurity spins by a field which might vary from impurity to impurity yields the following equation determining the superconducting transition temperature:

$$\ln\frac{T_c}{T_{c0}} = \frac{\pi}{2}T_c\sum_{n=-\infty}^{\infty}\left\{\frac{\operatorname{sign}\operatorname{Re}\eta_+}{\eta_+} + \frac{\operatorname{sign}\operatorname{Re}\eta_-}{\eta_-} - \frac{2}{|\omega_n|}\right\}, \quad (1)$$

$$\omega_n = (2n+1)\pi T_c.$$

$T_{c0}$ denotes the transition temperature of the superconductor in the absence of paramagnetic impurities. Extending appropriately the work by Gor'kov and Rusinov on ferromagnetism in supercondcuting alloys,[9,5] one finds that $\eta_+$ and $\eta_-$ are given by

$$\omega_\eta \pm iI = \eta_\pm - \frac{\langle S_z^2\rangle}{S^2}\frac{\operatorname{sign}\operatorname{Re}\eta_\pm}{\tau_{\text{ex}}} - \frac{1}{3\tau_{\text{s.o.}}}\frac{\eta_\mp - \eta_\pm}{\eta_\mp}\operatorname{sign}\operatorname{Re}\eta_\mp - F(\eta_\pm,\omega_n), \quad (2)$$

with

$$I \equiv c\langle S_z\rangle\langle J\rangle, \quad (3)$$

$$F(\eta_\pm,\omega_n) \equiv \int_{-\infty}^{\infty} dz\,\operatorname{sign}\operatorname{Re}\eta_\mp(z)\frac{\eta_\pm(\omega_n)+\eta_\mp(z)}{\eta_\mp(z)} \times K_\pm(\omega_n,z), \quad (4)$$

$$K_\pm(\omega_n,z) \equiv \frac{N(0)}{4p_{\text{F}}^2}\sum_\lambda\int\frac{d\Omega_q}{4\pi}\int_0^{q_c}dq\,q\int_{-\infty}^{\infty}\frac{dy}{2\pi}|J_\lambda(q,y)|^2 \times E_\lambda^{\pm}(q,y)\frac{f(z)(e^{z\beta}+e^{y\beta})}{i\omega_n - z - y} \quad (5)$$

$$q_c \equiv \min(2p_\mp, q_{\max}).$$

$\eta_\mp(\omega)$ is given by Eq. (2) if the replacements $\omega_n \to -i\omega$, $\eta_\pm \to -i\eta_\mp$, $\operatorname{sign}\operatorname{Re}\eta_\pm \to \operatorname{sign}\operatorname{Re}\eta_\mp$, and $F(\eta_\pm(\omega_n),\omega_n) \to F(-i\eta_\mp(\omega),-i\omega)$ are made. $S_z$ is the impurity-spin component in the direction of the average exchange field $\vec{\mathrm{I}}$. $\langle J\rangle$ denotes the average exchange-coupling matrix element. The electronic collision times $\tau_{\text{ex}}$ and $\tau_{\text{s.o.}}$ result from $s$-$d$ exchange scattering due to the impurity-spin component $S_z$ at zero temperature and from spin-orbit scattering, respectively. $N(0)$ is the normal-state density of states at the Fermi surface, $p_{\text{F}}$ is the Fermi momentum, $f(z)$ is the Fermi distribution function, and $J_\lambda(q,z)$ denotes the exchange-coupling matrix element taking into account screening of the exchange interaction between conduction electrons and paramagnetic impurities. Defining the impurity-spin propagator $E_\lambda(t) \equiv -i \times\langle T[S_-(t)S_+(0)]\rangle$, which describes the impurity-spin fluctuations, then $E_\lambda^+(t) \equiv E_\lambda(t<0)$ and $E_\lambda^-(t) \equiv E_\lambda(t>0)$ and their Fourier transforms are given by

$$E_\lambda^{\pm}(q,z) = -\frac{S(S+1)-\langle S_z^2\rangle \pm \langle S_z\rangle}{z-\omega_q^\lambda - \Sigma^\pm(q,z)}, \quad (7)$$

where the imaginary parts of the impurity-spin excitation self-energies $\Sigma^+$ and $\Sigma^-$ are positive and negative, respectively. $\langle S_z^2\rangle$ and $\langle S_z\rangle$ are given by

$$\langle S_z^2\rangle = S(S+1) - S\int_{-\infty}^{\infty}d\omega\,P(\omega)B_S(\beta\omega)\coth(\tfrac{1}{2}\beta\omega), \quad (8)$$

and

$$\langle S_z\rangle = S\int_{-\infty}^{\infty}d\omega\,P(\omega)B_S(\beta\omega). \quad (9)$$

$P(\omega)$ is the normalized distribution function of the impurity-spin Zeeman energies $\omega$. $P(\omega)$ takes into account the variation of the Zeeman energies from impurity spin to impurity spin and is often approximated by a Lorentzian function centered at the average spin-wave excitation energy $\omega_1$ and of width $\omega_2$ which is usually taken as a small fraction of $\omega_1$. It follows from the Ruderman-Kittel interaction between the paramagnetic impurities that

$$\omega_1 = \tfrac{2}{3}\gamma c N(0)\langle |J|^2\rangle S B_S(\beta\omega_1). \tag{10}$$

The constant $\gamma$ is of the order of unity.[10] For a ferromagnetic alloy one finds

$$\omega_1 = T_k/S, \tag{11}$$

where $T_k$ denotes the Curie temperature. Notice that for an Einstein spectrum $P(\omega)$ is given by the delta function $\delta(\omega-\omega_E)$.

Note that, in general, the superconducting transition temperature $T_c$ is now calculated from Eq. (1) after determining $\eta_\pm(\omega_n)$ numerically by Eq. (2), whereby $E_\lambda{}^\pm(q,z)$ might be approximated by replacing $\omega_q+\Sigma^\pm(q,z)$ by $\omega_1 \pm i\omega_2$, corresponding to a Lorentzian Zeeman energy distribution of width $\omega_2$ and centered at the average Zeeman energy $\omega_1$. Then Eq. (5) can approximately be rewritten as

$$K_\pm(\omega_n, z) = \frac{1}{2S^2\tau_{\text{ex}}}\frac{1}{2\pi}\left[\coth\left(\frac{\beta(\omega_1-i\omega_2)}{2}\right)\mp 1\right] S B_S(\beta(\omega_1-i\omega_2))\frac{f(z)\{e^{z\beta}+\exp[(\pm\omega_1\mp i\omega_2)\beta]\}}{i\omega_n - z\mp\omega_1\pm i\omega_2}. \tag{12}$$

Assuming that $\eta_\mp(z)$ is a function which varies smoothly with $z$, then $F(\eta_\pm,\omega_n)$ is approximately given by

$$F(\eta_\pm,\omega_n) = \frac{SB_S(\beta(\omega_1-i\omega_2))}{2S^2\tau_{\text{ex}}}\left[\coth\left(\frac{\beta(\omega_1-i\omega_2)}{2}\right)\mp 1\right]\operatorname{sign}\operatorname{Re}\eta_\mp(\omega_n)\frac{\eta_\pm(\omega_n)+\eta_\mp(\omega_n\pm i\omega_1\pm\omega_2)}{\eta_\mp(\omega_n\pm i\omega_1\pm\omega_2)}$$
$$\times\int_{\mathfrak{C}_\pm}\frac{dz}{2\pi}\frac{\exp[(\pm\omega_1\mp i\omega_2)\beta]}{i\omega_n - z} f(z\pm\omega_1\mp i\omega_2)[1+f(z)], \tag{13}$$

where the integration paths $\mathfrak{C}_\pm$ run at distance $-i\omega_2$ and $i\omega_2$, respectively, parallel to the real axis from $-\infty$ to $+\infty$. Combining then the second and fourth term on the right-hand side of Eq. (2), one finds that the $s$-$d$ exchange scattering is approximately represented by $-\operatorname{sign}\omega_n/S^2\tau_{\text{ex}}'$ as stated before. Equation (2) can then be solved approximately by

$$\frac{1}{\eta_\pm(\omega_n)} = \left[\omega_n + \operatorname{sign}\omega_n\left(\frac{\langle S_z{}^2\rangle}{S^2\tau_{\text{ex}}}+\frac{1}{3\tau_{\text{s.o.}}}\right)\mp iI\right]$$
$$\times\left[\left(|\omega_n| + \frac{S(S+1)-S\tanh(\beta\omega_1/2)B_S(\beta\omega_1)}{S^2\tau_{\text{ex}}}\right)\left(|\omega_n| + \frac{\langle S_z{}^2\rangle}{S^2\tau_{\text{ex}}}+\frac{1}{3\tau_{\text{s.o.}}}\right)+I^2\right]^{-1}, \tag{14}$$

which gives for small transition temperatures

$$\ln\frac{T_c}{T_{c0}} = 2\sum_{n=0}^{\infty}\left\{\frac{2n+1+[1+3(\tau_{\text{s.o.}}/\tau_{\text{ex}})]/3\pi\tau_{\text{s.o.}}T_c}{(2n+1+1/\pi\tau_{\text{ex}}T_c)[2n+1+(1+3\tau_{\text{s.o.}}/\tau_{\text{ex}})/3\pi\tau_{\text{s.o.}}T_c]+(I/\pi T_c)^2}-\frac{1}{2n+1}\right\}. \tag{15}$$

Starting with this solution for $\eta_\pm$, Eqs. (2) and (4) can be solved by iteration.

Notice that real electronic scattering as well as the anomalous $s$-$d$ scattering[7] by the paramagnetic impurities is negligible before ordering among the impurity spins starts, as comparison between experiment and theory shows, and, therefore, this will be even more so at lower temperatures for which ordering between the impurity spins occurs.

The superconducting transition temperature is now calculated by Eqs. (1), (2), (4), and (12), determining numerically $F(\eta_\pm,\omega_n)$ and $\eta_\pm(\omega_n)$. Figures 1 and 2 show the numerical results for the superconducting transition temperature and show also for comparison the experimental results.[4] The agreement between theory and experiment seems to be reasonable, particularly in view of the fact that not much detail is known at the present time about the impurity-spin ordering—for example, the varia-

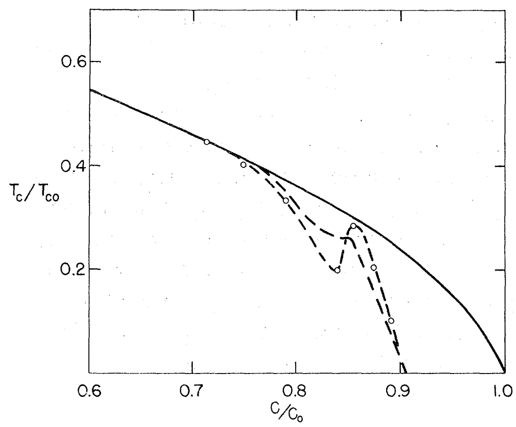


FIG. 1. The dependence of the reduced superconducting transition temperature on the concentration of paramagnetic impurities is shown for the alloy $La_{3-x}Gd_xIn$. The transition temperature $T_{c0}$ refers to the superconductor in the absence of paramagnetic impurities. The critical concentration $c_0 = 2.15$ at.%, the $s$-$d$ collision time $\tau_{ex}$, and the solid curve are determined from

$$\ln\frac{T_c}{T_{c0}} = \psi(\tfrac{1}{2}) - \psi\left(\tfrac{1}{2} + 0.140\frac{T_{c0}}{T_c}\left[\frac{c}{c_0}\right]\right)$$

by fitting the experimental results at low impurity concentrations, where the impurity spins are free to rotate. $\psi$ denotes the digamma function. The dashed curve with the circles shows the experimental results.[4] The other dashed curve results from theory taking into account ordering among the impurity spins which was assumed to occur for concentrations above $c = 0.8c_0$. We used $S = \frac{7}{2}$; the average exchange field $I = 2.51 \times 10^{-2}(c/c_0)(T_{c0}/T_c)$, corresponding to $J = 3°K$; the spin-orbit collision time $\tau_{s.o.} = 0.09\tau_{ex}$; the average Zeeman energy $\omega_1 = 2.05c$ (°K); and $\omega_2 = 0.2\omega_1$.

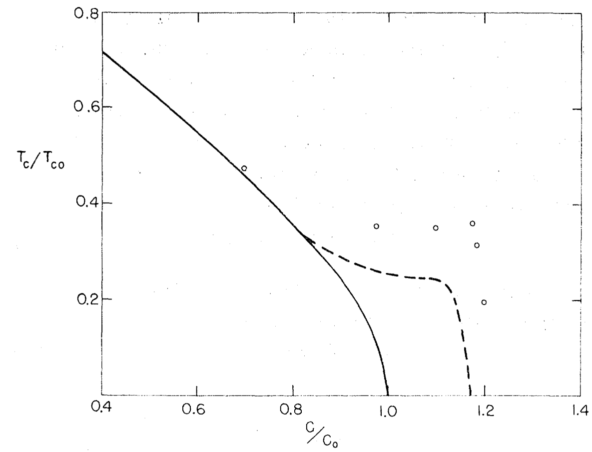


FIG. 2. The dependence of the superconducting transition temperature on the concentration of paramagnetic impurities is shown for the alloy $La_{1-x}Gd_x$. The notation is the same as for Fig. 1. The critical concentration $c_0 = 0.82$ at.%, the collision time $\tau_{ex}$, and the solid curve are determined as described in the text for Fig. 1. The circles indicate the experimental results. The dashed curve results from the theory assuming that ordering among the impurity spins occurs for impurity concentrations above $c = 0.9c_0$. We used $S = \frac{7}{2}$; the average exchange field $I = 1.5 \times 10^{-2}(c/c_0)(T_{c0}/T_c)$, corresponding to $J = 2.5°K$; the spin-orbit collision time $\tau_{s.o.} = 0.03\tau_{ex}$; the average Zeeman energy $\omega_1 = 1.71c$ (°K); and $\omega_2 = 0.2\omega_1$.

tion of the exchange field fixing the impurity spins throughout the crystal. Therefore, it would be of interest to study in detail the dependence of the reduction in the electronic spin-flip scattering on the distribution of the impurity-spin Zeeman energies. In this way it might turn out to be possible to distinguish between ferromagnetic and antiferromagnetic ordering of the impurity spins.

The results obtained show clearly that the gliding of the Fermi surface arising from the average exchange field $I$, which would cause a rapid decrease in the superconducting transition temperature, depends sensitively on spin-orbit scattering. It seems that for the alloy $La_{3-x}Gd_xIn$, spin-orbit scattering is too weak to prevent the gliding of the Fermi surface due to $I$. Furthermore, the Fermi surface gliding becomes effective at lower impurity concentrations than the reduction in the spin-flip scattering (which tends to increase the transition temperature). For the alloy $La_{1-x}Gd_x$, spin-orbit scattering seems to be strong enough to prevent the gliding of the Fermi surface up to higher paramagnetic impurity concentrations and, consequently, the reduction in the electronic spin-flip scattering becomes effective first. One sees that the change in the superconducting transition temperature which results from ordering among the impurity spins is determined by the interplay of spin-orbit scattering, reduction of spin-flip scattering, and gliding of the Fermi surface.

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