Sensitivity of the critical magnetic field to phase shifts of paramagnetic impurities

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We have calculated the critical magnetic field deviation function $D(t)$ of a BCS superconductor containing paramagnetic impurities treated in the strong-scattering limit of Shiba and of Rusinov. For certain combinations of scattering phase shifts the variation of $D(t)$ with impurity concentration can be very different from that found in the Abrikosov-Gor'kov approximation. This is observed in experiments on Zn-Mn which can be understood qualitatively on the basis of recent phase shifts derived from tunneling experiments.

I. INTRODUCTION

Recent tunneling experiments[1–4] support the existence of localized excited states associated with magnetic impurities in superconductors. This phenomenon is predicted by the theory of Shiba[5] and of Rusinov[6] (SR). The SR theory allows for strong coupling between conduction electrons and magnetic ions, as opposed to the perturbative treatment of Abrikosov and Gor'kov[7] (AG), which is valid only when the interaction is weak.

Theoretical examinations[8–12] of the thermodynamic properties of impure superconductors within the SR formalism have generally used the assumption that S-wave scattering will be dominant. However, both band-structure calculations[13] and tunneling experiments by Ginsberg and others[1–4] indicate that contributions from S-, P-, and D-wave scattering may be significant for many materials. In particular, Terris and Ginsberg[4] have deduced scattering parameters (ϵ_l, $l=0,1,2$) for Zn-Mn alloys from tunneling experiments. This is of special interest because the critical magnetic field measurements of Smith[14] for these same alloys show significant deviations from the predictions of AG theory. The results of Smith will be shown to be at least in qualitative agreement with SR theory.

In Sec. II we present a brief discussion of the calculation of the critical magnetic field using the real-frequency-axis version of SR theory in the BCS limit. This is followed in Sec. III by a summary of some general results involving the critical field and the deviation function $D(t)$ for one and two partial waves. Section IV is concerned with the Zn-Mn alloys, and conclusions follow in Sec. V.

II. CALCULATION

The real-axis version of the Eliashberg equations with the SR treatment of paramagnetic impurities has been given by Schachinger and Carbotte.[15] In the BCS limit they are

$$\Delta(\omega)Z(\omega)=N_0V\int_0^{\omega_D'}d\omega'\,\mathrm{Re}\left[\frac{\Delta(\omega')}{[\omega'^2-\Delta^2(\omega')]^{1/2}}\right]\tanh\left[\frac{\beta\omega'}{2}\right]-i\frac{\Delta(\omega)}{[\omega^2-\Delta^2(\omega)]^{1/2}}\sum_l(2l+1)\alpha_l\frac{\epsilon_l}{1+\epsilon_l}\left[\frac{\omega^2-\Delta^2(\omega)}{\omega^2-\epsilon_l^2\Delta^2(\omega)}\right], \tag{1}$$

$$[1-Z(\omega)]\omega=-i\frac{\omega}{[\omega^2-\Delta^2(\omega)]^{1/2}}\sum_l(2l+1)\alpha_l\left[\frac{1}{1+\epsilon_l}\right]\left[\frac{\omega^2-\Delta^2(\omega)}{\omega^2-\epsilon_l^2\Delta^2(\omega)}\right]. \tag{2}$$

Here $\Delta(\omega)$ is the complex gap function, $\beta=1/k_BT$, where T is absolute temperature, and N_0V is the usual BCS coupling constant. The impurity parameters ϵ_l are given by $\epsilon_l=\cos(\delta_l^+-\delta_l^-)$, where $\delta_l^{+(-)}$ are the phase shifts for the lth partial wave for spin-up (-down) electrons. One also has $\alpha_l=(n_I/2\pi N_0)(1-\epsilon_l^2)$, where n_I is the paramagnetic impurity concentration and N_0 is the electronic density of states at the Fermi surface for one spin. The quantity $\alpha=\sum_l(2l+1)\alpha_l$ is analogous to the pair-breaking parameter of AG theory.

Using the definition $u(\omega)=\omega/\Delta(\omega)$, and for the order parameter

$$\Delta(\alpha,T)=N_0V\int_0^{\omega_D'}d\omega\,\mathrm{Re}\left[\frac{\Delta(\omega)}{[\omega^2-\Delta^2(\omega)]^{1/2}}\right]\times\tanh\left[\frac{\beta\omega}{2}\right],$$

one may rewrite (1) and (2) to obtain

$$\Delta(\alpha,T)=N_0V\int_0^{\omega_D'}\mathrm{Re}\left[\frac{1}{(u^2-1)^{1/2}}\right]\tanh\left[\frac{\beta\omega}{2}\right] \tag{3}$$

and

$$\omega=u\Delta(\alpha,T)-i\frac{u}{(u^2-1)^{1/2}}\sum_l(2l+1)\alpha_l\left[\frac{u^2-1}{u^2-\epsilon_l^2}\right]. \tag{4}$$

Here, $\omega_D'=[\omega_D^2+\Delta^2(\alpha,T)]^{1/2}$, where ω_D is the Debye energy. Equations (3) and (4) may be solved numerically for the order parameter as well as the function $u(\omega)$ [equivalent to the gap function $\Delta(\omega)$].

Note that if (4) is written in terms of the real and imaginary parts of $u(\omega)=u_1(\omega)+iu_2(\omega)$, and separated into two equations [the real and imaginary parts of (4)], then the imaginary part of Eq. (4) depends only implicitly on ω. This allows one to find numerically u_2 as a function of u_1 for given $\Delta(\alpha,T)$. This may then be used in the real part of (4) to find the corresponding frequency ω by direct substitution. Once values of u_1, u_2, and ω are known for the appropriate frequency range, they may be used in (3) to complete one iteration for the order parameter. The procedure is then repeated for this new value of $\Delta(\alpha,T)$. The number of iterations of (3) required for convergence of the order parameter was decreased significantly through the adoption of a method proposed by Sprung and Vallières[16] to accelerate the convergence of Hartree-Fock calculations of nuclear structure.

Once the order parameter has converged, this and the function $u(\omega)$ from the last iteration of (3) may be used to find the difference in free energy between the superconducting and normal states. The result of Skalski *et al.*[17] for the free-energy difference is

$$\frac{F_S-F_N}{N_0}=-\int_0^{\omega_D'}\left[\frac{N(\omega)}{N_0}-1\right]\left[2\omega\tanh\left[\frac{\beta\omega}{2}\right]+\frac{4}{\beta}\left[\ln(1+e^{-\beta\omega})+\frac{\beta\omega}{e^{\beta\omega}+1}\right]\right]+\Delta^2(\alpha,T)\left[\frac{1}{N_0V}-1\right], \tag{5}$$

where

$$\frac{N(\omega)}{N_0}=\mathrm{Re}\left[\frac{u(\omega)}{[u^2(\omega)-1]^{1/2}}\right]$$

is the quasiparticle density of states in the superconductor. Later we will correlate the zero-frequency limit of $N(\omega)$, as a function of impurity concentration, with the behavior of the critical magnetic field.

The critical magnetic field is given in the usual way by $H_c^2/8\pi=F_N-F_S$. The deviation function is also defined, as usual, by

$$D(t)=[H_c(t)]/[H_c(0)]-(1-t^2),$$

where $t=T/T_c$.

III. DEVIATION FUNCTION IN SR THEORY

One conventionally plots $D(t)$, the deviation of $H_c(t)/H_c(0)$ from the parabola $1-t^2$, to illustrate the dependence of the critical magnetic field on temperature and impurity concentration. Figure 1 indicates the two extreme cases possible in SR theory. Figure 1(a) is the AG limit, $\epsilon_0=1$ (the value actually used was $\epsilon_0=0.995$ for reasons of programming expediency). Decker and Finnemore[18] have previously shown such curves for values of the reduced pair-breaking parameter α/α_c between 0 and approximately 0.75. Their measured results for Th-Gd alloys agree well with AG theory for concentrations up to 0.2 at.% Gd, corresponding to $\alpha/\alpha_c=0.6$. They were not able to examine higher Gd concentrations due to experimental difficulties.

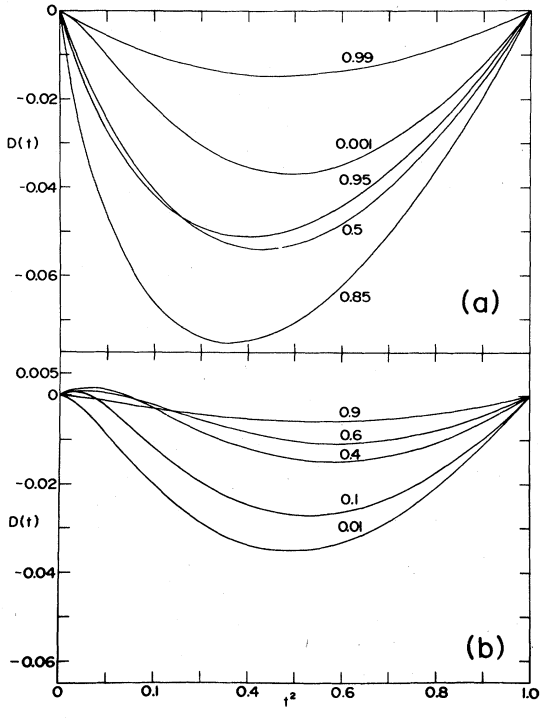

FIG. 1. (a) Deviation function for several different impurity concentrations with scattering parameter $\epsilon_0=0.995$ (the AG limit). The curves are labeled by reduced impurity concentration α/α_c, where α_c is the critical value of the pair-breaking parameter. (b) Deviation function for several impurity concentrations for $\epsilon_0=0.001$.

In agreement with the results of Decker and Finnemore,[18] we find that the minimum of $D(t)$ decreases to roughly -0.07 for $\alpha/\alpha_c=0.85$. However, we also find that for still higher concentrations the minimum of the curve rapidly increases toward zero. This interesting behavior coincides roughly with the onset of gaplessness at zero temperature, which occurs for $\alpha/\alpha_c=0.91$ in AG theory. It will be established later in this section that a nonzero density of states at zero frequency is always correlated in SR theory with the minimum of $D(t)$ being an increasing function of impurity concentration.

The other extreme case possible within SR theory is illustrated in Fig. 1(b), which is a set of $D(t)$ curves for $\epsilon_0=0.001$. In this case the minimum of $D(t)$ is a monotonically increasing function of impurity concentration, in striking contrast with the AG results. One may also note that in this limit the density of states at zero frequency is nonzero for any finite impurity concentration; that is, the material is always gapless.

The remainder of this section will be concerned with the deviation function for different scattering parameters in SR theory, including both S- and P-wave scattering as well as the S-wave results already described. The general behavior can most clearly be seen by plotting the value of $D(t)$ at one particular reduced temperature t as a function of impurity concentration, rather than plotting full $D(t)$ curves. The temperature $t=0.7$ was arbitrarily chosen because the minimum of the curves is generally found near $t^2=0.5$. Figure 2(a) contains several curves of $D(0.7)$ versus α/α_c for different scattering parameters. The corresponding densities of states at zero frequency, $N(0)/N_0$, are plotted in Fig. 2(b).

Several general observations may be made upon examination of Fig. 2. Perhaps the most important and interesting observation concerns a correlation between the slope of $D(0.7)$ versus α/α_c in Fig. 2(a) and the slope of $N(0)/N_0$ versus α/α_c in Fig. 2(b). When $N(0)$ is zero, then $D(0.7)$ is a decreasing function of impurity concentration. However, when $N(0)/N_0$ increases rapidly, then $D(0.7)$, as a function of α/α_c, also has a large positive slope. This correlation indicates that the low-frequency part of the density of states $N(\omega)$ is dominant in determining the details of the thermodynamics of SR superconductors.

This last statement is also supported by the observation that, when more than one partial wave is considered, scattering parameters ϵ_l near 1 are relatively ineffective in changing the $D(t)$ curves. For example, in Fig. 2(a) the curve for $\epsilon_0=0.01,\epsilon_1=0.9$ is significantly closer to the curve for $\epsilon_0=0.01$ than the curve $\epsilon_0=0.01,\epsilon_1=0.6$. If one examines the full density-of-states curves $N(\omega)$ for these examples, one sees that adding a scattering parameter $\epsilon_1=0.9$ to the value $\epsilon_0=0.01$ results in major changes only for ω near $\Delta(\alpha,T)$, the order parameter. In fact, as the second scattering parameter approaches 1, the density of states differs from that for $\epsilon_0=0.01$ only for ω very near $\Delta(\alpha,T)$. Thus, the curves of $N(\omega)/N_0$ for $\omega\ll\Delta(\alpha,T)$ and therefore also $D(t)$ are nearly identical for $\epsilon_0=0.01$ and for $\epsilon_0=0.01,\epsilon_1=0.99$.

One may also note that, when two partial waves are included, both the $D(0.7)$ and $N(0)$ curves in Fig. 2 lie between the curves which result when the same numerical values ϵ_0,ϵ_1 are used for S-wave scattering only. Furthermore, although this is not shown in Fig. 2, these curves are quite insensitive to the interchange of scattering parameters. For example, the curves for $\epsilon_0=0.01,\epsilon_1=0.6$ and those for $\epsilon_0=0.6,\epsilon_1=0.01$ are nearly indistinguishable.

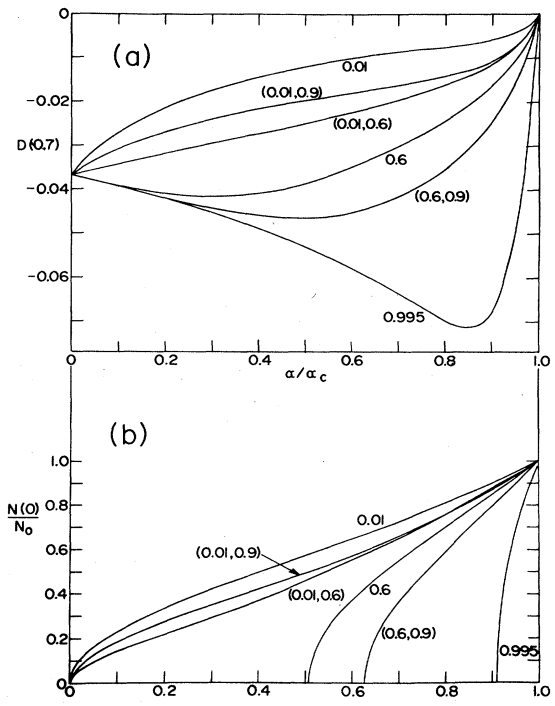

FIG. 2. (a) Deviation function at reduced temperature $t=0.7$ as a function of reduced impurity concentration α/α_c. The curves are labeled by the scattering parameters. The single number c implies $\epsilon_0=c$, and a pair (c,d) implies $\epsilon_0=c$, $\epsilon_1=d$. (b) Density of states at zero frequency as a function of reduced impurity concentration for the same set of scattering parameters as in (a).

IV. CRITICAL FIELDS OF Zn-Mn ALLOYS

Smith[14] has measured critical magnetic fields for a series of Zn-Mn alloys. The results were found to differ significantly from the predictions of AG theory. These deviations were believed to be due to the existence of states within the superconducting energy gap, but no comparison was made with a theory which allows this effect to be included.

More recently, Terris and Ginsberg[4] have analyzed the tunneling characteristics of Zn-Mn alloy films in terms of SR theory. They extracted two sets of parameters ϵ_l, $l=0,1,2$ which fit their experimental conductances reasonably well. We have calculated $H_c(t)$ using these two sets of parameters and find at least qualitative agreement with the experimental results of Smith.[14]

The most notable feature of our $D(t)$ curves is the fact

that for both sets of parameters the curves initially become more negative as the Mn concentration increases, followed by an increase toward zero at higher concentrations. Figure 3(a) shows some $D(t)$ curves for the set of scattering parameters which Ginsberg calls density of states I (DOS I): $\epsilon_0=1.00$, $\epsilon_1=0.53$, and $\epsilon_2=0.94$. In this case the minimum of $D(t)$ stays between -0.03 and -0.04 for impurity concentrations between 0% and more than 60% of the critical concentration.

Figure 3(b) consists of $D(t)$ curves for the second set of parameters, DOS II, which is $\epsilon_0=0.25$, $\epsilon_1=0.50$, and $\epsilon_2=1.0$. In this case the minimum of $D(t)$ remains between -0.02 and -0.04 for concentrations between 0% and more than 50% of the critical concentration. Although the amount of scatter in the data of Smith makes a detailed comparison impossible, both sets of scattering parameters give $D(t)$ curves which agree at least qualitatively with the experimental results. The same thing cannot be said for AG theory; the $D(t)$ curves of Smith do not become sufficiently negative to agree at all with the AG results of Fig. 1(a).

Another comparison may be made by examining the relationship between $H_c(0)$ and T_c through the quantity $\tilde{H}^2=H_c^2(0)/\gamma T_c^2$. Here γ is the coefficient of the linear term in the electronic specific heat for the pure material. Figure 4 shows the data of Smith to be significantly different from the AG prediction, but at least in qualitative agreement with the predictions of SR theory using Ginsberg's parameters. Also included in Fig. 4 is a curve for a set of scattering parameters calculated by Kunz and Ginsberg[13] ($\epsilon_0=0.951$, $\epsilon_1=0.842$, and $\epsilon_2=0.998$). Terris and Ginsberg[4] found that these values give significantly worse agreement with their measured tunneling characteristics than do DOS I and DOS II. Our calculation shows that these calculated scattering parameters also give critical fields which are in worse agreement with the measurements of Smith than DOS I and DOS II.

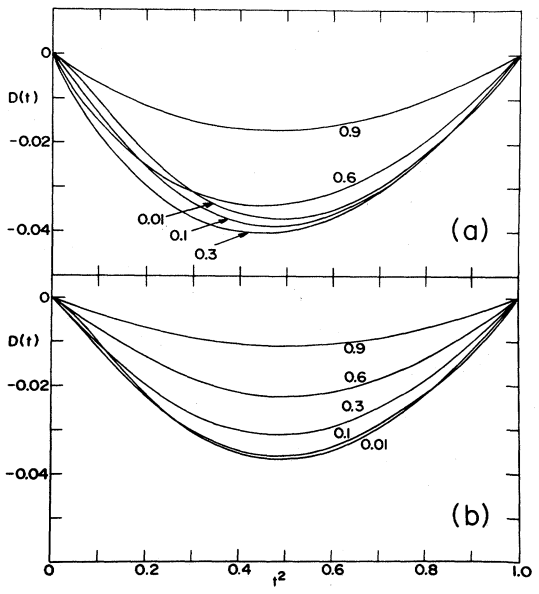

FIG. 3. (a) Several $D(t)$ curves for the set of scattering parameters DOS I ($\epsilon_0 1.00$, $\epsilon_1=0.53$, and $\epsilon_2=0.94$). The curves are labeled by reduced impurity concentration, α/α_c. (b) Some $D(t)$ curves for the scattering parameters DOS II ($\epsilon_0=0.25$, $\epsilon_1=0.50$, and $\epsilon_s=1.0$), labeled as in (a).

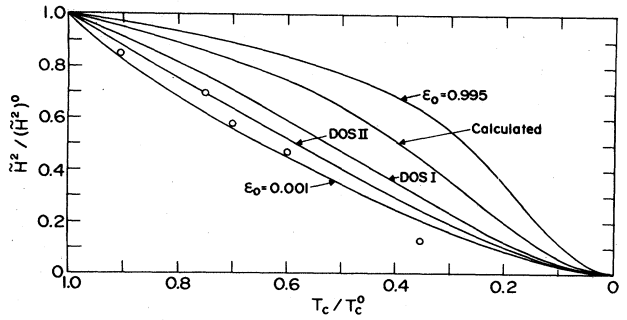

FIG. 4. Law of corresponding states. $\tilde{H}^2=H_c^2(0)/\gamma T_c^2$. The superscript 0 refers to a value for the pure material. Included are curves for DOS I ($\epsilon_0=1.00$, $\epsilon_1=0.53$, and $\epsilon_2=0.94$), DOS II ($\epsilon_0=0.25$, $\epsilon_1=0.50$, and $\epsilon_2=1.0$), as well as a curve labeled "calculated" which refers to the band-structure-derived set of parameters ($\epsilon_0=0.951$, $\epsilon_1=0.842$, and $\epsilon_2=0.998$). The circled points are the experimental values of Smith. Curves for $\epsilon_0=0.001$ and 0.995 (the AG limit) are also included.

V. CONCLUSIONS

We have numerically solved the real-frequency-axis version of the BCS equations with paramagnetic impurities in the SR formalism, and have found the critical magnetic fields. The change in the deviation function $D(t)$ with impurity concentration is found to be correlated with the zero-frequency density of states $N(0)$. When $N(0)$ is zero, then the minimum of $D(t)$ decreases with increasing impurity concentration. When $N(0)$ is nonzero, then the minimum of $D(t)$ increases with increasing impurity concentration. Furthermore, the more rapid the increase in $N(0)$, the more rapid the rise of the minimum of $D(t)$ toward zero with increasing impurity concentration.

Critical fields have been calculated for Zn-Mn alloys using scattering parameters determined by Terris and Ginsberg[4] from tunneling experiments. The results are found to be in qualitative agreement with the critical field measurements of Smith.[14]

Finally, one can safely say that the thermodynamic properties of superconductors with magnetic impurities in the SR formalism *do* vary significantly with the scattering parameters. Therefore, thermodynamic measurements may be a useful adjunct to tunneling experiments in attempts to estimate more accurately appropriate scattering parameters for real alloys.

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