Narrowing of ESR lines by an exchange field in a superconductor

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An analysis is made of narrowing of inhomogeneously and dipole-broadened ESR lines by a long-range exchange in a superconductor. The mechanism of this narrowing differs qualitatively from the well-known Anderson-Weiss mechanism when narrowing is due to a rapid exchange of states between spins which are in different local fields. In the present case a dynamic coupling between spins is provided by an exchange field, which alters greatly the narrowing behavior. A simple formula is derived for the width of an exchange-narrowed ESR line: it generalizes the familiar Anderson-Weiss formula and combines the field and fluctuation narrowing effects. Estimates are obtained of the magnitude of the narrowing and these are used to account for the strong narrowing of an ESR line as a result of the superconducting transition in the LaEr system. A numerical analysis is made of the resonance line profile and it is shown that the line asymmetry as a result of the field narrowing increases the asymmetry of the detected ESR signal, as found experimentally.

1. INTRODUCTION

Experiments on electron spin resonance (ESR) of localized moments of Er^{3+} in the cubic phase of La revealed a strong narrowing of the resonance line directly below the superconducting transition temperature T_c (Ref. 1). This was an unexpected effect because the temperature-dependent contribution to the ESR line width is due to the exchange scattering of conduction electrons by magnetic impurities and it should increase as a result of the superconducting transition because of the coherence effects and because of an increase in the density of the electron states at the energy gap edge. Such broadening of a magnetic resonance line has been observed a long time ago in NMR experiments[2] and has apparently been confirmed by the first ESR experiments.[3,4] Rettori *et al.*[3] put forward the idea and Kosov and Kochelaev[5] carried out a calculation showing that relaxation of a localized moment to conduction electrons (Korringa relaxation) may be blocked as a result of the superconducting transition under the electron bottleneck conditions, when the bottleneck of the relaxation process is the transfer of magnetization from conduction electrons to the lattice. This transfer is due to the spin-orbit scattering of electrons which, in contrast to the exchange interaction, is reduced strongly by the superconducting transition.

However, this mechanism cannot account for the experimental results reported in Ref. 1, because the narrowing observed for the Er concentration of 2 at.% was approximately twice as large as the whole contribution of the Korringa mechanism to the line width at $T = T_c$. Moreover, the observation that the slope of the temperature dependences of the line width in the normal phase was practically independent of the Er concentration indicated the absence of the bottleneck in the normal phase and this implied the absence of the necessary condition for the blocking of the Korringa relaxation as a result of the superconducting transition. On the other hand, the large "residual width" of the line (found by extrapolation to $T = 0$ of the temperature dependence of the line width in the normal phase) indicated a considerable contribution of the inhomogeneous and dipole mechanism to the total ESR line width and the dependence of the narrowing on the Er ion concentration was evidence of the importance in the narrowing process of those spin-spin interactions in which the conduction electron system is participating because only this system is affected by the phenomenon of superconductivity.

It was shown in Refs. 1 and 6 that an indirect exchange interaction of localized moments via conduction electrons changes at the superconducting transition and it can be represented by two terms, the first of which is the usual Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction:

$$\mathscr{H}_{ex}^{RKKY} = \frac{1}{2}\sum_{i\neq j} J_{ij}^{RKKY}\mathbf{S}_i\mathbf{S}_j,$$

$$J_{ij}^{RKKY} = \frac{\pi\varepsilon_F\rho_F^2 J_{sf}^2}{2k_F^3}\frac{\cos 2k_F r_{ij}}{r_{ij}^3}\exp\left(-\frac{r_{ij}}{l_p}\right); \quad (1)$$

the second term is the long-range interaction of antiferromagnetic nature which appears only in the superconducting phase:

$$\mathscr{H}_{ex}^{s} = \frac{1}{2}\sum_{i\neq j} J_{ij}^{s}\mathbf{S}_i\mathbf{S}_j,$$

$$J_{ij}^{s} = \frac{1}{r_{ij}}\frac{3}{2}\left(\frac{\pi\rho_F J_{sf}}{k_F}\right)^2 T\sum_{\omega}\frac{1}{1+u^2}\frac{\gamma}{l_p}$$

$$\times\exp\left\{-\frac{r_{ij}}{l_p}\left[\frac{\Delta(1+u^2)^{1/2}}{\varepsilon_F}k_F l_p - \frac{2l_p}{3l_s}\frac{2u^2+1}{1+u^2} + \frac{4l_p}{3l_{so}}\right]^{1/2}(3\gamma)^{1/2}\right\}, \quad (2)$$

$$\gamma = 1 - \frac{l_p}{l_s} + \frac{\Delta(1+u^2)^{1/2}}{\varepsilon_F}k_F l_p + \frac{l_p}{l_{so}}, \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|;$$

here, ρ_F is the density of the electron states at the Fermi level ε_F; J_{sf} is the s-f exchange integral; k_F is the Fermi momen-

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tum; l_p, l_s, and l_{s0} is the mean free path of conduction electrons governed respectively by the scattering involving a change in the momentum, the scattering by magnetic impurities, and the spin-orbit scattering; $\Delta(T)$ is the order parameter of the superconductor; T is the absolute temperature; $u \equiv u(\omega)$ is the dimensionless parameter of the Abrikosov-Gorkov theory of superconductors which contain paramagnetic impurities (see, for example, Ref. 7)

The potential J^s_{ij} has a range of the order of the coherence length of the superconductor $\xi \ll a_0$ (a_0 is the lattice constant); in the case of intermetallics the typical values are $\xi \gtrsim 100$–150 Å (Ref. 4). Next, the usual analysis leads to the Anderson-Weiss theory[8] of the narrowing of ESR lines subject to exchange: $\mathscr{H}^{\rm RKKY}_{\rm ex} + \mathscr{H}^s_{\rm ex}$. However, the results of calculations indicate that $\mathscr{H}^s_{\rm ex}$ makes a negligible contribution to the frequency of exchange fluctuations of local fields and, consequently, it does not alter the line width. This is due to the fact that the narrowing condition in the Anderson-Weiss theory actually requires that the exchange between spins in a selected pair at distances important in a given system should be greater than the dipole fields created by the spins at their mutual positions in the dipole broadening case or greater than the difference between the precession frequencies of these spins in the inhomogeneous broadening case. On the other hand, an estimate of the constant J^s_{ij} for the nearest neighbors in the lattice shows that this constant is $(k_F\xi)^2 \gtrsim 10^4$ times smaller than the RKKY exchange constant of Eq. (1) and much smaller than any characteristic energy of the system (Larmor frequency, dipole or inhomogeneous width), representing a fraction of a gauss in units of the field.

We shall show below that, in spite of the extremely small value of the constant, the exchange term $\mathscr{H}^s_{\rm ex}$ of Eq. (2) reduces the inhomogeneous and dipole widths of an ESR line. The mechanism and pattern of the narrowing are very different from those in the Anderson-Weiss theory. In the second section we shall solve the model problem of narrowing of an inhomogeneous distribution of local fields by the long-range exchange of Eq. (2) and establish a qualitative pattern and mechanism of the narrowing, which we shall call the field narrowing (for a brief account see Ref. 9). In the third section we shall solve the problem of the exchange narrowing of an inhomogeneously broadened ESR line by the combined effect of the RKKY exchange of Eq. (1) and the exchange $\mathscr{H}^s_{\rm ex}$ of Eq. (2). In the fourth section we shall give the results of a solution of the problem of the exchange narrowing of a dipole-broadened ESR line and in the fifth section we shall discuss experiments carried out on the LaEr system.[1]

2. PROCESS OF NARROWING OF AN INHOMOGENEOUS ESR LINE BY AN EXCHANGE FIELD IN A SUPERCONDUCTOR

We shall determine whether the long-range exchange $\mathscr{H}^s_{\rm ex}$ of Eq. (2) can narrow an ESR line by considering first a model in which magnetic impurities are coupled only by the exchange $\mathscr{H}^s_{\rm ex}$. We shall assume that these impurities are distributed at random between the lattice sites and that the local precession frequency is $\omega_s + \Omega_i$. In the presence of static and alternating external magnetic fields the Hamiltonian of the system is of the form

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_{loc} + \mathscr{H}_{ex}{}^s + \mathscr{H}_{es} + \mathscr{H}_1(t),$$
$$\mathscr{H}_0 = \omega_s \sum_i S_i{}^z, \qquad \mathscr{H}_{loc} = \sum_i \Omega_i S_i{}^z,$$
$$\mathscr{H}_{es} = -J_{sf} \sum_i \mathbf{S}_i \boldsymbol{\sigma}(\mathbf{r}_i),$$
$$\mathscr{H}_1(t) = -\frac{1}{2} \sum_i (S_i{}^+ \omega_1{}^-(t) + S_i{}^- \omega_1{}^+(t)), \tag{3}$$
$$\omega_1{}^\pm(t) = \omega_1 \exp(\pm i\omega t),$$
$$\boldsymbol{\sigma}(\mathbf{r}_i) = \frac{1}{N} \sum_{\mathbf{q}} \exp(-i\mathbf{q}\mathbf{r}_i)\, \boldsymbol{\sigma}_{\mathbf{q}}.$$

Here, $\boldsymbol{\sigma}(\mathbf{r}_i)$ is the spin density of conduction electrons at the ith lattice site; $\mathbf{r}_i$ is the radius vector of this site; $\boldsymbol{\sigma}_{\mathbf{q}}$ is the Fourier component of the spin density of conduction electrons; S^α_i is the αth component of the spin moment of an impurity at the site i; $\mathscr{H}_0$ and $\mathscr{H}_{\rm loc}$ are the Zeeman energy operators of magnetic impurities in external and local fields, respectively; N is the number of lattice sites per unit volume; $\mathscr{H}_1(t)$ describes the interaction of the spin system of impurities with an alternating field of amplitude ω_1 and frequency ω. The cause of the homogeneous broadening is the interaction between the impurity spins and conduction electrons via the s-f exchange (Korringa mechanism) described by $\mathscr{H}_{es}$.

As pointed out in the Introduction, the range of the "superconducting" exchange of Eq. (2) is of the order of the coherence length ξ of a superconductor, which we shall assume to be much greater than the spatial scale of inhomogeneities of the precession frequency Ω_i. In this case the problem can be solved as spatially homogeneous although it remains spectrally inhomogeneous with a local field distribution function $g(\Omega)$. In view of the smallness of the exchange constant and its special dependence on the distance, the spectral width of the frequencies of the exchange fluctuations due to $\mathscr{H}^s_{\rm ex}$ is very small ($\lesssim 1$ G), so that we shall describe the kinetics of an inhomogeneously broadened spectrum in the language of spin packets which are sets of impurity spins precessing at similar frequencies. We shall write down the transport equation for the transverse magnetization of a spin packet

$$M_n{}^- = \sum_{i \in \{n\}} M_i{}^-,$$

retaining the first order in respect of the exchange $\mathscr{H}^s_{\rm ex}$ (in the form of a molecular field and neglecting fluctuations[10]) and terms up to the second order in $\mathscr{H}_{es}$, describing the Knight shift and the relaxation to electrons. The method used to describe the transport equations within the formalism of the nonequilibrium density matrix is described in detail in the literature (see, for example, Refs. 11 and 12) so that we shall not repeat the procedure here. After going over to a continuous distribution of the frequencies in such packets, the transport equation for the transverse component of the spectral density of the magnetization of the localized moments is

$$\frac{dM^-(\Omega)}{dt}=-i\{\tilde{\omega}_s+\Omega+\Delta_{ex}-iT_{se}^{-1}\}(M^-(\Omega)-\omega_1^-(t)g(\Omega)\chi_s)$$
$$+i\Delta_{ex}g(\Omega)\int_{-\infty}^{\infty}M^-(\Omega)\,d\Omega, \qquad (4)$$
$$\Delta_{ex}=\langle S^z\rangle \sum_j{}' J_{ij}^s; \qquad (5)$$

in Eq. (4), $\tilde{\omega}_s=\omega_s(1+J_{sf}\chi^e/Ngg_e)$ is the precession frequency in an external field subject to the Knight shift; χ^e is the spin susceptibility of conduction electrons in a superconductor; χ_s is the static susceptibility of the magnetic impurities; g and g_e are the g factors of the impurity moments and electrons, respectively; T_{se}^{-1} is the Korringa rate of relaxation of impurities to conduction electrons. The sum with a prime is taken over the sites occupied by the impurity moments.

The first term on the right-hand side of Eq. (4) describes precession of the spectral density of the magnetization in an internal field consisting of a static external field $\tilde{\omega}_s$, a local field Ω, and an internal exchange field Δ_{ex} of Eq. (5); it also describes the relaxation to conduction electrons. The second term is due to the relationship between the spectral density of the magnetization $M^-(\Omega)$ and the nonequilibrium magnetization of the rest of the local frequency spectrum. The most important feature is that, in contrast to similar cross-relaxation equations in which the transport coefficient is real and represents the rate of cross relaxation or jumps, the transport coefficient in Eq. (4) is purely imaginary $[ig(\Omega)\Delta_{ex}]$; this means that the magnetizations in different parts of the inhomogeneous spectrum are coupled by dynamic molecular fields. This circumstance alters fundamentally the narrowing effect.

The solution of Eq. (4) gives the dynamic susceptibility

$$\chi^-(\omega)=\chi_s\left\{1-\omega\int_{-\infty}^{\infty}\frac{g(\Omega)\,d\Omega}{\omega-\tilde{\omega}_s-\Delta_{ex}-\Omega+iT_{se}^{-1}}\right\}$$
$$\times\left\{1+\Delta_{ex}\int_{-\infty}^{\infty}\frac{g(\Omega)\,d\Omega}{\omega-\tilde{\omega}_s-\Delta_{ex}-\Omega+iT_{se}^{-1}}\right\}^{-1} \qquad (6)$$

In the case of a rectangular distribution of the local fields $g(\Omega)=1/\gamma$ (for Ω within the range from $-\gamma/2$ to $\gamma/2$), the susceptibility $\chi^-(\omega)$ can be investigated analytically and the qualitative pattern of the exchange-field narrowing can be determined. In this case the integral is readily found to be

$$\int_{-\infty}^{\infty}\frac{g(\Omega)\,d\Omega}{\omega-\tilde{\omega}_s-\Delta_{ex}-\Omega+iT_{se}^{-1}}$$
$$=-\frac{1}{\gamma}\ln\left(\frac{\omega-\tilde{\omega}_s-\Delta_{ex}+iT_{se}^{-1}-\gamma/2}{\omega-\tilde{\omega}_s-\Delta_{ex}+iT_{se}^{-1}+\gamma/2}\right). \qquad (7)$$

If the condition $|\Delta_{ex}|\gg T_{se}^{-1},\gamma$ is satisfied near the frequency $\omega=\tilde{\omega}$, the susceptibility (6) can be reduced to

$$\chi^-(\omega)\approx\chi_s\frac{\tilde{\omega}_s+\Delta_{ex}-iT_{se}^{-1}-(\gamma/2)^2(3\Delta_{ex})^{-1}}{\tilde{\omega}_s-\omega-iT_{se}^{-1}-(\gamma/2)^2(3\Delta_{ex})^{-1}} \qquad (8)$$

and it then describes a mode with a resonance field

$$g\mu_B H_{coll}\approx\omega+(\gamma/2)^2(3\Delta_{ex})^{-1}, \qquad (9)$$

which is slightly smaller than the resonance field of the center of gravity of an inhomogeneously broadened spectrum [$\Delta_{ex}\leqslant 0$, see Eq. (5)]. However, the resonance of Eq. (9) is not the only one in the system under consideration. An expansion of the logarithm in Eq. (7) for $\omega\approx\tilde{\omega}_s+\Delta_{ex}$ in terms of the small ratio $(\tilde{\omega}_s-\omega+\Delta_{ex}-iT_{se}^{-1})(\gamma/2)^{-1}$ gives the following expression for the susceptibility

$$\chi^-(\omega)\approx\chi_s\left\{\frac{\tilde{\omega}_s+\Delta_{ex}}{\Delta_{ex}}-\left(\frac{\gamma/2}{\Delta_{ex}}\right)^2\right.$$
$$\left.\times\,\tilde{\omega}_s\left[\omega-\tilde{\omega}_s-\Delta_{ex}+iT_{se}^{-1}+\frac{(\gamma/2)^2}{\Delta_{ex}}\right]^{-1}\right\}. \qquad (10)$$

Equation (10) shows that there is another mode with a resonance field

$$g\mu_B H_{sat}\approx\omega-\Delta_{ex}+(\gamma/2)^2\Delta_{ex}^{-1}. \qquad (11)$$

The intensity of a resonance in Eq. (11), which we shall call a satellite, amounts to $(\gamma/2\Delta_{ex})^2\ll 1$ of the intensity of a resonance (9), which we shall call the collective mode. Therefore, the ESR spectrum observed under field narrowing conditions when $|\Delta_{ex}|\gg T_{se}^{-1},\gamma$ consists of a strong collective mode and a low-intensity satellite shifted away from the collective mode by an amount equal to the exchange field (in the direction of higher fields, because $\Delta_{ex}\leqslant 0$).

The molecular field Δ_{ex} can be expressed conveniently in terms of the paramagnetic Curie temperature due to the exchange term $\mathscr{H}_{ex}^s$ $(T\gg\tilde{\omega}_s)$:

$$\Delta_{ex}=\tilde{\omega}_s\frac{\theta^s(T)}{T},\qquad \theta^s(T)=-\frac{S(S+1)}{3}\sum_j{}' J_{ij}^s. \qquad (12)$$

The substitution of J_{ij}^s from Eq. (2) into Eq. (12) yields the following expression for $\theta^s(T)$:

$$\theta^s(T)=-S(S+1)\frac{4\pi}{3}n\left(\frac{\pi\varepsilon_F\rho_F^2J_{sf}^2}{2k_F^3}\right)\left(1-\frac{\chi^e}{\chi_n^e}\right), \qquad (13)$$

where χ_n^e is the spin susceptibility of conduction electrons in the normal phase; n is the number of impurities per unit volume.

In the case of more realistic distribution functions $g(\Omega)$ the susceptibility of Eq. (6) can be investigated in detail by means of a computer. Figure 1 illustrates the process of narrowing of the distribution of local fields of Gaussian form by the exchange field. Analytic and numerical investigations show that the qualitative picture of the exchange-field narrowing is completely different from the picture of the usual exchange narrowing[8] in which the initial ESR spectrum contracts to its center of gravity, becoming narrower and more symmetric. In the field narrowing case the initial spectrum becomes deformed, even if it is symmetric (Fig. 1), so that the high-field wing of the ESR line is now stronger than the low-field wing. Below the superconducting transition temperature T_c the exchange field rises:

$$\Delta_{ex}\propto T^{-1}(1-\chi^e/\chi_n^e),$$

as demonstrated in Eq. (12), and the collective mode gradu-

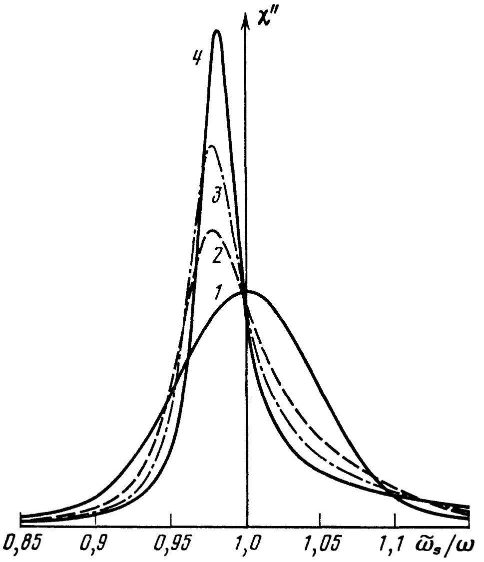

FIG. 1. Profile of an ESR line $\chi'' = \mathrm{Im}\chi^-(\omega)$ plotted for different values of the ratio of the exchange field Δ_{ex} to the half-width Γ of the Gaussian distribution function of local fields $X = |\Delta_{ex}|/\Gamma$: 1) $X = 0$; 2) 1.0; 3) 1.5; 4) 2.0; $\Gamma/\omega = 0.05$; homogeneous width $T_{se}^{-1} = 0.2\Gamma$ selected to be the same for all the curves and the intensities are plotted in arbitrary units.

ally becomes narrower. We can see from Fig. 1 that in the case of smooth distributions the satellite is practically unresolved and it manifests itself by an asymmetry of the resonance line. It should be pointed out that a maximum of $\mathrm{Im}\chi^-(\omega)$ is shifted somewhat away from the resonance field at the center of gravity of the spectrum in the direction opposite to the shift of the satellite, so that the common center of gravity of the collective mode and of the satellite remains unshifted. This is a natural consequence of commutation of the scalar exchange $\mathscr{H}_{ex}^s$ of Eq. (2) with any component of the total spin of the impurities.

The possibility of narrowing of the hyperfine structure of an ESR line by the field coupling in the normal phase is considered in Ref. 13. However, it should be pointed out that the molecular field approximation which works very well in the case of the long-range exchange of Eq. (2) is quite unsuitable for the RKKY exchange of Eq. (1), for which an *rms* fluctuation of the exchange field is almost an order of magnitude higher than its average value (see, for example, Refs. 10 and 14). Therefore, in the normal phase the effects associated with the presence of an average exchange field should be correspondingly small (to what degree, we shall find later).

3. EXCHANGE NARROWING OF AN INHOMOGENEOUSLY BROADENED ESR LINE IN A SUPERCONDUCTOR

We shall now return to the problem of the role of the RKKY exchange of Eq. (1), which has been dropped from the model considered above. At magnetic impurity concentrations of the order of 1 at. % the exchange narrowing effects become important in the normal phase. The profile of an exchange-narrowed line is Lorentzian and its half-width is[8]

$$(\Delta\omega)_{AW} \sim M_2/\omega_{ex}, \tag{14}$$

where ω_{ex} is the half-width of the spectral distribution of the frequencies of the exchange fluctuations of the impurity spins. An estimate shows that the exchange field Δ_{ex}, which appears below the superconducting transition temperature, is of the same order as ω_{ex} so that the field narrowing and the usual fluctuation exchange narrowing both appear in a superconductor. Therefore, the problem of the field narrowing of an ESR line already narrowed by the RKKY exchange in the normal phase is of practical interest. In this case all the localized moments are coupled by the strong RKKY exchange to form a single moment so that we can select the transverse components of the total magnetization as the variables in the reduced description. The transport equation is obtained by the nonequilibrium density matrix method[11,12]; this equation is of the Bloch type and in the Fourier representation in time domain it is

$$-i\omega M^-(\omega) = -i(\tilde{\omega}_s - iT_{se}^{-1})(M^-(\omega) - \chi_s\omega_1) - M^-(\omega)K^-(\omega), \tag{15}$$

where

$$K^-(\omega) = \int_{-\infty}^{0} dt e^{-i\omega t} K^-(t), \tag{16}$$

$$K^-(t) = \int_0^1 d\tau e^{\varepsilon t} \left\langle \frac{\langle \rho_0^{-\tau}[S^+, \mathscr{H}_{loc}](t)\rho_0^{\tau}[\mathscr{H}_{loc}, S^-]\rangle}{\langle S^+S^-\rangle} \right\rangle_{conf};$$

$[\ldots](t)$ represents the Heisenberg bracketing by exponential functions with the Hamiltonian $\mathscr{H}_0 = \mathscr{H}_{ex}^s + \mathscr{H}_{ex}^{RKKY}$; $S^\pm$ are the transverse components of the total impurity spin;

$$\rho_0 = \exp[-(\mathscr{H}_0 + \mathscr{H}_{ex}^s + \mathscr{H}_{ex}^{RKKY})/T],$$

$\langle\ldots\rangle$ is the equilibrium thermodynamic averaging; $\langle\ldots\rangle_{conf}$ is the configurational averaging. The substitution of $\mathscr{H}_{loc}$ from Eq. (3) and integration with respect to t and τ gives

$$\Gamma(\omega) = \mathrm{Re}\, K^-(\omega) = \frac{1}{2} M_2 G(-\omega),$$
$$R(\omega) = \mathrm{Im}\, K^-(\omega) = \frac{1}{2\pi} M_2 \int_{-\infty}^{\infty} G(\omega_1)\frac{d\omega_1}{\omega+\omega_1}, \tag{17}$$

where

$$M_2 = \int_{-\infty}^{\infty} \Omega^2 g(\Omega)\, d\Omega$$

is the second moment of the distribution of the local fields $g(\Omega)$, and $G(\omega)$ is the Fourier transform of the correlation function averaged over the configurations

$$G_j(t) = \langle S_j^+(t)S_j^-\rangle / \langle S_j^+S_j^-\rangle.$$

We can find the approximation for this function by expanding it as a commutator series in terms which are quadratic in time:

$$G_j(t) = \frac{\langle S_j^+(t)S_j^-\rangle}{\langle S_j^+S_j^-\rangle} \approx \exp\{i\tilde{\omega}_s t + i\Delta_{ex}t - t^2\omega_j^2\}. \tag{18}$$

Here, Δ_{ex} is the first moment of the correlation function (18) which is dominated by the long-range exchange $\mathscr{H}_{ex}^s$. Direct calculations show that Δ_{ex} is exactly the molecular field of Eqs. (5) and (12), which is the reason for the reduction in the inhomogeneous width of an ESR line in a model discussed in the preceding section; ω_j^2 is proportional to the second moment of the correlation function, when the main contribution to ω_j^2 comes from the RKKY exchange of Eq. (1):

$$\omega_j^2 = \sum_i{}' \omega_{ij}^2 = \frac{S(S+1)}{3}\left(\frac{\pi\varepsilon_F\rho_F^2 J_{sf}^2}{2k_F^3}\right)^2 \times \sum_i{}' \left[\frac{\cos 2k_F r_{ij}}{r_{ij}^3}\exp\left(-\frac{r_{ij}}{l_p}\right)\right]^2. \quad (19)$$

The normalized correlation function (18) for a dilute paramagnet depends on the configuration of the immediate neighbors and this changes from site to site. Averaging over the configurations in the case of low impurity concentrations ($\leqslant$10 at.%) gives rise to the following kinetics (for details see Refs. 14 and 15):

$$G(t) = \langle G_j(t)\rangle_{conf} \approx \exp(i\tilde{\omega}_s t + i\Delta_{ex} t) F(t),$$
$$F(t) = \exp\left\{-n\int dV_i [1-\exp(-t^2\omega_{ij}^2)]\right\}. \quad (20)$$

If we ignore the decay of the RKKY exchange in a distance equal to the mean free path of conduction electrons l_p, we find that the integral in Eq. (20) can be calculated and it gives the exponential kinetics:

$$F(t) = \exp(-\omega_{ex}^0 |t|),$$
$$\omega_{ex}^0 \approx \frac{2}{3}\pi^2\left(\frac{\pi S(S+1)}{6}\right)^{1/2}\left(\frac{\rho_F^2 J_{sf}^2 \varepsilon_F n}{k_F^3}\right), \quad (21)$$

from which the Lorentzian profile of the frequency transform $G(\omega)$ can be deduced. We calculated the kinetics of Eq. (20) numerically for various mean free paths of conduction electrons in order to allow for the exponential cutoff of the RKKY exchange. The kinetics is nonexponential, but Fourier transformation of the kinetics shows that the profile of the correlation function (18) is close to Lorentzian up to frequencies somewhat greater than the half-width at half-amplitude; in the wings the frequency dependence is weaker than ω^{-2}. Since we are interested in frequencies right up to the half-width of the correlation function, we shall approximate the line profile by a Lorentzian curve of equivalent half-width ω_{ex}:

$$G(\omega) \approx 2\omega_{ex}[(\omega+\tilde{\omega}_s+\Delta_{ex})^2+\omega_{ex}^2]^{-1}. \quad (22)$$

Numerical fitting shows that ω_{ex} is very accurately an exponential function of the mean free path:

$$\omega_{ex} \approx \omega_{ex}^0 \exp(-1{,}91 N_l^{-1/3}), \quad (23)$$

where $N_l = (4\pi/3) l_p^3 n$ is the number of impurities in a sphere of radius equal to the mean free path of conduction electrons. Equations (17) and (20)–(23) allow us to obtain the following expressions for the real and imaginary parts of $K^-(\omega)$:

$$\Gamma(\omega) = \frac{M_2\omega_{ex}}{(\omega-\tilde{\omega}_s-\Delta_{ex})^2+\omega_{ex}^2},$$
$$R(\omega) = \frac{M_2(\omega-\tilde{\omega}_s-\Delta_{ex})}{(\omega-\tilde{\omega}_s-\Delta_{ex})^2+\omega_{ex}^2}. \quad (24)$$

Therefore, part of the last term in Eq. (15) [proportional to $\Gamma(\omega)$] which determines the line width is a product of two bell-shaped functions shifted relative to one another by the exchange field Δ_{ex} (Fig. 2). Since the exchange narrowing condition postulates that the inequality $\omega_{ex} \gg M_2^{1/2} \gg M_2/\omega_{ex}$ is obeyed, the curve $\Gamma(\omega)$ is much wider than the $\chi''(\omega) = \mathrm{Im}\chi^-(\omega)$ curve, so that in the first approximation we can ignore the change in $\Gamma(\omega)$ within the limits of the ESR line width, taking it at the frequency $\omega = \tilde{\omega}_s$. Consequently, the contribution of the inhomogeneous broadening narrowed by the exchange fluctuations and the exchange field is

$$(\Delta\omega)_s \approx \frac{M_2\omega_{ex}}{\omega_{ex}^2+\Delta_{ex}^2} = M_2 \,\mathrm{Re}\left(\frac{1}{\omega_{ex}+i\Delta_{ex}}\right). \quad (25)$$

Clearly, if we ignore the exchange field ($\Delta_{ex} = 0$), Eq. (25) reduces to the Anderson-Weiss formula of Eq. (14). It also follows from Eq. (25) that in the normal phase, when the average exchange field Δ_n due to the RKKY exchange is small ($\Delta_n \lesssim 0.1\omega_{ex}$), the field narrowing effects are weak.

The solution of Eq. (15) gives the dynamic susceptibility

$$\chi^-(\omega) = \chi_s \frac{-(\tilde{\omega}_s - iT_{se}^{-1})}{\omega-\tilde{\omega}_s-R(\omega)+i(T_{se}^{-1}+\Gamma(\omega))}. \quad (26)$$

The ESR line profile $\chi''(\omega) = \mathrm{Im}\chi^-(\omega)$ is shown in Fig. 2 for different values of the exchange field Δ_{ex} when a resonance is traversed by a magnetic field. It is clear from this figure that the initial line profile ($\Delta_{ex} = 0$, continuous curve), which is of Lorentzian form, becomes asymmetric under the field-narrowing conditions and, exactly as in Fig. 1, the high-field wing of the line is stronger.

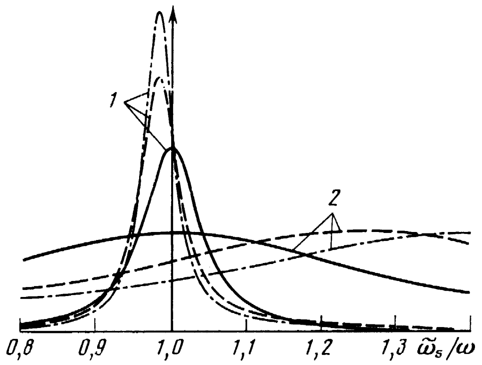

FIG. 2. Profile of an exchange-narrowed ESR line $\chi'' = \mathrm{Im}\chi^-(\omega)$ (curves denoted by 1) and form of the correlation function $\Gamma(\omega) = \mathrm{Re}K^-(\omega)$ (curves denoted by 2) plotted for different values of the ratio of the exchange field Δ_{ex} to the frequency ω_{ex} of the exchange fluctuations $Y = |\Delta_{ex}|/\omega_{ex}$: $Y = 0$ corresponds to the continuous curves, and $Y = 0.67$ to the dashed curves, and $Y = 1.0$ to chain curves. These curves are plotted for the following values of the parameters: $M_2/\omega = 0.01$, $\omega_{ex}/\omega = 0.3$, $T_{se}^{-1}/\omega = 0.0075$, narrowing coefficient $k = \omega_{ex}/M_2^{1/2} = 3$. The intensities are plotted in arbitrary units.

4. EXCHANGE NARROWING OF THE DIPOLE WIDTH OF AN ESR LINE IN A SUPERCONDUCTOR

The dipole-dipole interaction of paramagnetic impurities is, together with inhomogeneities of the local fields, the main source of the residual width of an ESR line. Therefore, in this section we shall estimate the influence of the long-range exchange $\mathscr{H}_{ex}^s$ on the dipole line width (for a preliminary estimate see Ref. 16).

The Hamiltonian of the problem is

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_{dd}+\mathcal{H}_{ex}^{\rm RKKY}+\mathcal{H}_{ex}^{s}+\mathcal{H}_{es}+\mathcal{H}_1(t),$$

$$\mathcal{H}_{dd}=\frac{1}{2}\sum_{i\neq j}A_{ij}S_i^zS_j^z, \quad (27)$$

$$A_{ij}=\frac{3}{2}\frac{g^2\mu_B^2}{r_{ij}^3}(1-3\cos^2\theta_{ij}),$$

and the other terms are given by Eqs. (1)–(3). As in the case of an inhomogeneously broadened line, we shall assume that in the normal phase the ESR line is exchange-narrowed by the RKKY interaction and we shall write down the transport equations for the transverse components of the total magnetic moment of paramagnetic impurities. This equation can also be obtained by the Zubarev method and in the Fourier representation it is analogous to Eq. (15):

$$-i\omega M^-(\omega)=-i\{\tilde{\omega}_s+\Delta\omega_d-iT_{se}^{-1}\}$$
$$\times(M^-(\omega)-\chi_s\omega_1)-M^-(\omega)K^-(\omega), \quad (28)$$

$$\Delta\omega_d=\langle S^z\rangle\sum_i{}' A_{ij}.$$

The frequency shift $\Delta\omega_d$ depends on the shape of the sample and in the case of small values of $\langle S^z\rangle \ll S$ and spherical samples it is very small. Moreover,

$$K^-(\omega)=\int_{-\infty}^{0}e^{-i\omega t}K^-(t)\,dt,$$
$$(29)$$
$$K^-(t)=\int_0^1 d\tau e^{\varepsilon t}\left\langle\frac{\langle\rho_0^{-\tau}[S^+,\mathcal{H}_{dd}](t)\rho_0^{\tau}[\mathcal{H}_{dd},S^-]\rangle}{\langle S^+S^-\rangle}\right\rangle_{conf}.$$

The substitution of $\mathcal{H}_{dd}$ from Eq. (27) and a calculation of the integrals yield formulas for which we have to know the correlation function:

$$Q^-(t)=\left\langle\frac{\langle(S_i^+S_j^z)(t)(S_i^-S_j^z)\rangle}{\langle S_i^+S_i^-\rangle}\right\rangle_{conf}. \quad (30)$$

We shall estimate this function on the basis of the following considerations. We shall select a spin i and its neighbors at a site j creating a local dipole field at the ith spin. Since the environment of the spin j contains many other spins, it follows that fluctuations of the dipole field due to the RKKY exchange of this spin with its environment is actually independent of the exchange with the spin i (with the obvious exception of the case when the spins i and j are an isolated pair, but the statistical weight of such pairs is small and they do not contribute to the absorption at frequencies of the order of the half-width of the ESR line).[17] This consideration allows us to separate the correlation function:

$$\langle\langle(S_i^+S_j^z)(t)(S_i^-S_j^z)\rangle\rangle_{conf}$$
$$\approx\langle\langle S_i^+(t)S_i^-\rangle\rangle_{conf}\langle\langle S_j^z(t)S_j^z\rangle\rangle_{conf}. \quad (31)$$

The method for the calculation of the correlation functions is described above and the results of the calculation are as follows:

$$\langle\langle S_j^z(t)S_j^z\rangle\rangle_{conf}/\langle\langle S_j^zS_j^z\rangle\rangle_{conf}\approx\exp\{-\omega_{ex}|t|\}. \quad (32)$$

The Fourier transform of the correlation function and the contribution to the line width are described by

$$Q^-(\omega)\approx\frac{2\omega_{ex}^*}{(\omega+\tilde{\omega}_s+\Delta_{ex})^2+(\omega_{ex}^*)^2}, \quad (33)$$

$$(\Delta\omega)_s\approx\frac{M_2\omega_{ex}^*}{(\omega_{ex}^*)^2+\Delta_{ex}^2}=M_2\,\mathrm{Re}\left(\frac{1}{\omega_{ex}^*+i\Delta_{ex}}\right). \quad (34)$$

Here, $\omega_{ex}^*=2\omega_{ex}$ [see Eq. (25)] and

$$M_2=\frac{9}{20}(g\mu_B)^4 n\sum_{j(\neq i)}r_{ij}^{-6}$$

is the second moment for the dipole interaction (averaged over the angles for the spin 1/2). This estimation method is simplest in the context of the present paper, but we have carried out calculations in which the correlation function (30) was expanded directly as a commutator series and we also obtained estimates by the method of moments. In the former case we obtained a result identical with Eqs. (33) and (34), which justifies decoupling of the correlation function (31). The method of moments gave also a similar estimate.

5. DISCUSSION OF RESULTS

We shall now consider in detail the experimental data of Ref. 1. For 2% Er in La the narrowing at the superconducting transition is approximately one-third of the residual width of the ESR line. If we assume that the narrowing is due to a mechanism considered in the present paper, the exchange field has to be $\Delta_{ex}\approx 0.73\omega_{ex}$.

Equations (12), (13), (21), and (23) allow us to compare Δ_{ex} and ω_{ex}:

$$\frac{|\Delta_{ex}|}{\omega_{ex}}=g\left|\frac{g_J-1}{g_J}\right|\frac{\tilde{\omega}_s}{T}\left[\frac{6\tilde{S}(\tilde{S}+1)}{\pi}\right]^{1/2}\left(1-\frac{\chi^e}{\chi_n^e}\right)$$
$$\times\exp(1.91N_l^{-1/4})\approx 0.67\left(1-\frac{\chi^e}{\chi_n^e}\right), \quad (35)$$

where g_J is the Landé g factor and $\tilde{S}$ is the effective spin of the ground crystal multiplet. The estimate given by Eq. (35) is obtained on the assumption that the ESR data of LaEr are as follows[1]: $g\approx 6.8$, $g_J=6/5$, $\tilde{\omega}_s\approx 0.45$ K, $T\approx 2.8$ K, $\tilde{S}=1/2$, $N_l\approx 5$. The susceptibility $\chi^e(T)$ of a superconductor with singlet pairing becomes considerably smaller than χ_n^e if a sample is cooled (see Refs. 4 and 7).

Narrowing of the dipole width is less, because $\omega_{ex}^*=2\omega_{ex}$. Equations (14) and (25) [or (14) and (34)] readily yield

$$(\Delta\omega)_{AW}-(\Delta\omega)_S=M_2\frac{\Delta_{ex}^2}{\omega_{ex}^2+\Delta_{ex}^2}, \quad (36)$$

which shows that the narrowing is proportional to the impurity concentration if the broadening is inhomogeneous (which is frequently true); it vanishes at $T=T_c$ ($\Delta_{ex}\to 0$), as found in the experiments (see Fig. 7 in Ref. 1).

We must point out an additional important factor. It was reported in Ref. 1 that the profile of the derivative of the absorbed power differs from that for a Lorentzian line and this is manifested by a reduction of the ratio of the amplitudes of the low- and high-field peaks of the signal, known as the asymmetry parameter A/B, from the value in the normal phase $(A/B)_n\approx 2.55$ which falls to $(A/B)_s\approx 1.7$ (see the

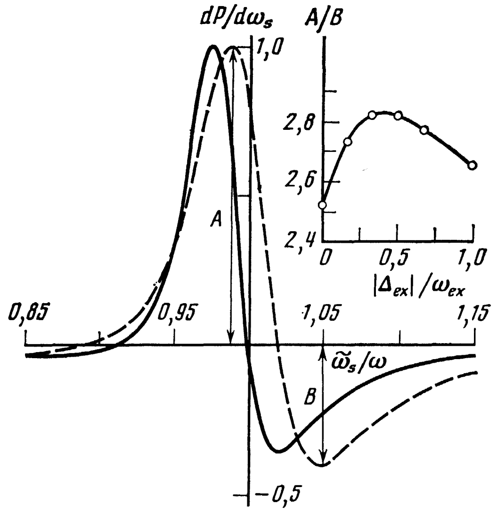

FIG. 3. Field derivative $dP/d\omega_s$ plotted as a function of the microwave power absorbed by a bulk sample for different values of the ratio $Y=|\Delta_{ex}|/\omega_{ex}$: $Y=0$ is represented by the dashed curve and it corresponds to $A/B=2.52$; $Y=0.5$ is represented by the continuous curve and it corresponds to $A/B=2.81$. The values of the parameters M_2, and T_{se}^{-1} are the same as in Fig. 2. The curves are normalized to the sample amplitude of the low-field peak. The inset shows the dependence of the asymmetry parameter A/B on Y.

data for 0.5 at.% Er in Fig. 4 of Ref. 1). The deviation is greatest at the lowest Er concentration and when this concentration is increased, the ratio A/B rises. It is known[18] that the screening of an alternating field by nondissipative supercurrents in a superconductor increases the relative contribution of χ'' to the absorbed power $P(\omega_s)$ compared with the normal phase for which we have $P(\omega_s)\propto(\chi'+\chi'')$. Moreover, the asymmetric distribution of the magnetic field in an Abrikosov vortex lattice also distorts the ESR line.[19] These two factors reduce strongly the parameter A/B in the superconducting phase to 1–1.3, which is demonstrated by practically all the experiments carried out on samples with low impurity concentrations in the range $\lesssim 0.1$ at.% (see Ref. 4).

We can determine the influence of the χ'' asymmetry due to the field narrowing on the ESR signal profile by calculating $dP/d\omega_s$, but taking a mixture of χ' and χ'' with the same weight so as to exclude all other factors that might affect A/B. Such calculations show (Fig. 3) that an increase in the exchange field (i.e., lowering of the temperature below T_c and/or an increase in the paramagnetic impurity concentration) increases the asymmetry parameter from 2.52 for $\Delta_{ex}=0$ to 2.81 for $\Delta_{ex}\approx 0.5\omega_{ex}$.

It therefore follows that the ESR line asymmetry due to the field narrowing prevents a reduction in A/B by supercurrents and by vortical distribution of the magnetic field, in agreement with the experimental results. We are of the opinion that this is an additional evidence in support of the narrowing by the exchange field, and is the reason why the ESR line width decreases as a result of the superconducting transition in LaEr.

Finally, we shall point out that far from the superconducting temperature the increasing inhomogeneity of the field in an Abrikosov lattice and the associated inhomogeneity of the exchange field Δ_{ex} hinder the field narrowing process giving rise to a plateau in the temperature dependence of the ESR line width.[1]

[1]N. E. Alekseevskiĭ, I. A. Garifullin, B. I. Kochelaev, and É. G. Kharakhash'yan, Zh. Eksp. Teor. Fiz. 72, 1523 (1977) [Sov. Phys. JETP **45**, 799 (1977)].
[2]L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959)
[3]C. Rettori, D. Davidov, P. Chaikin, and R. Orbach, Phys. Rev. Lett. **30**, 437 (1973).
[4]K. Baberschke, Z. Phys. B **24**, 53 (1976).
[5]A. A. Kosov and B. I. Kochelaev, Zh. Eksp. Teor. Fiz. **74**, 148 (1978) [Sov. Phys. JETP **47**, 75 (1978)].
[6]B. I. Kochelaev, L. R. Tagirov, and M. G. Khusainov, Zh. Eksp. Teor. Fiz. **76**, 578 (1979); **79**, 333 (1980) [Sov. Phys. JETP **49**, 291 (1979); **51**, 826 (1980)].
[7]K. Maki, in: Superconductivity (ed. by R. D. Parks), Vol. 2, Marcel Dekker, New York (1969), p. 1035.
[8]P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 269 (1953).
[9]B. I. Kochelaev, L. R. Tagirov, and K. F. Trutnev, Proc. Twenty-Second AMPERE Congress, Zurich, 1984, ed. by K. A. Muller, R. Kind, and J. Roos, publ. by Zurich Ampere Committee, Zurich (1984), p. 301.
[10]L. R. Tagirov and G. G. Khaliullin, Fiz. Tverd. Tela (Leningrad) **24**, 1649 (1982) [Sov. Phys. Solid State **24**, 941 (1982)].
[11]V. A. Atsarkin and M. I. Rodak, Usp. Fiz. Nauk **107**, 3 (1972) [Sov. Phys. Usp. **15**, 251 (1972)].
[12]L. L. Buishvili, M. D. Zviadadze, and G. R. Khitsishvili Zh. Eksp. Teor. Fiz. **54**, 876 (1968) [Sov. Phys. JETP **27**, 469 (1968)].
[13]S. E. Barnes, J. Phys. F **4**, 1535 (1974).
[14]R. E. Walstedt and L. R. Walker, Phys. Rev. B **9**, 4857 (1974).
[15]M. R. McHenry, B. G. Silbernagel, and J. H. Wernick, Phys. Rev. B **5**, 2958 (1972).
[16]B. I. Kochelaev, N. G. Koloskova, and A. A. Kosov, in: Magnetic Resonance and Related Phenomena (Proc. Twentieth AMPERE congress, Tallinn, 1978, ed. by E. Kundla, E. Lippmaa, and T. Saluvere), Springer Verlag, Berlin (1979), p. 209.
[17]E. S. Grinberg, B. I. Kochelaev, and G. G. Khaliullin, Fiz. Tverd. Tela (Leningrad) **23**, 397 (1981) [Sov. Phys. Solid State **23**, 224 (1981)].
[18]B. I. Kochelaev and M. G. Khusainov, Zh. Eksp. Teor. Fiz. **80**, 1480 (1981) [Sov. Phys. JETP **53**, 759 (1981)].
[19]R. Orbach, Phys. Lett A **47**, 281 (1974).

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