Nuclear-resonance line shapes due to magnetic impurities in metals

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A general formulation is presented for the calculation of static field distributions caused by randomly placed impurities in a lattice. Specific evaluations are carried out for the case of combined Ruderman-Kittel-Kasuya-Yosida (RKKY) and dipolar interactions between magnetic impurities and host nuclei. In this case the line shape is shown to approach a Lorentzian in the limit of great dilution, in agreement with earlier theories for the dipolar case. Analytic expressions for the half-widths are given. The Lorentzian shape is shown to be a consequence of the R^{-3} range dependence (i.e., to hold only in this case) and to hold also for an arbitrary distribution of impurity-moment values. These results are corroborated by explicit machine computations for the concentration range $0.01 \leq c \leq 1.0$ at.%, in which no approximations of a serious nature are introduced. The linewidth law for combined RKKY and dipolar coupling is derived and verified. This technique is applied to the problem of line narrowing due to resistivity damping of the RKKY oscillations, obtaining a damping length greater by a factor of ~ 2 than that originally deduced by Heeger, Klein, and Tu. The self-damping of RKKY oscillations by the Mn impurities in *Cu* Mn is estimated to be significant for $c \gtrsim 1$ at.%. Further applications are discussed.

I. INTRODUCTION

Over the past 15 years or so, the study of magnetic or nearly magnetic impurities in metals has attracted the interest of numerous solid-state theorists and experimentalists. Among the many phenomena which characterize these systems are the conduction-electron spin-density oscillations generated by such impurities in the surrounding host metal, which we henceforth refer to as Ruderman-Kittel-Kasuya-Yosida (RKKY) oscillations.[1,2] One of the important experimental manifestations of these oscillations is the broadening of host nuclear-magnetic-resonance (NMR) lines through hyperfine coupling with the perturbed spin density.[3] In fact, this phenomenon provides the only feasible method for measuring this effect at large distances from the impurity. It is the primary concern of this paper to calculate the breadth and shape of NMR lines broadened in this manner.

In dilute alloys, it is the long-range ($r \gg a$; a is the lattice constant) portion of the spin-density oscillations which is sampled by the NMR linewidth. Fortunately, it is just this region that is most reliably calculated by available theories, whether formulated in terms of direct and "mixing" impurity-host exchange couplings[2,4] or in terms of scattering phase shifts.[5] It is especially important, then, to be able to draw accurate inferences about spin-density-oscillation amplitudes from linewidth data.

The RKKY line-shape problem has been a matter of interest for over a decade; only recently, however, has the correct answer begun to emerge via the "successive-convolution" technique developed by Mizuno[6] and Alloul.[7] In the earliest theories, emphasis was placed on the "one-impurity" nature of the broadening. Behringer[8] calculated an approximate line shape by simply making a histogram of all the RKKY amplitudes which occur within a sphere that contains, on the average, one impurity. Chapman and Seymour[9] modified the statistics to ensure that no other impurities are nearer the site sampled than the one considered. This change reduced the broadening coefficient a factor of 4 below Behringer's. In more recent work[6,7,10] it was realized that one must consider the effect of many impurities in order to get an accurate linewidth, which was then found to lie between those of Refs. 8 and 9.

Although the successive-convolution method is statistically correct at low concentrations, we develop here an alternate formulation which we believe has several advantages. (i) It automatically handles higher concentrations. (ii) It gives, in some cases, an approximate analytic form for the line shape. (iii) We feel it is less cumbersome for computational purposes. Our method is based on a statistical formulation of the random-impurity problem due to Markoff[11] and is also the starting point of Anderson's treatment[12] of dilute dipolar broadening, as well as Cohen and Reif's discussion[13] of quadrupolar broadening due to random crystalline imperfections.

After a brief description of the formulation in Sec. II, we apply it in Sec. III to the problem of broadening due to the combined effect of RKKY and direct dipolar interactions. Both approximate calculations for the limit of high dilution and direct machine evaluations of the full line shape over a range of concentrations are presented. Our results are compared with those of previous theories. In Sec. IV these methods are applied to the case of impurity-damped RKKY oscillations first investi-

gated (for the system Cu_xAl_{1-x}: Mn) by Heeger, Klein, and Tu.[14] Our results and conclusions are summarized in Sec. V.

II. BASIC FORMULATION

The linewidth calculation begins with the assumptions (a) that the impurities are randomly distributed, and (b) that each site i in the lattice, when occupied with a magnetic impurity, produces at the origin a frequency shift ω which is static, (i.e., not time varying) but which varies randomly with a (normalized) distribution $p_i(\omega)$ over an ensemble of such sites. Any motion of the impurities is thus assumed to be either fast or slow compared with the time scale set by the inverse of the NMR linewidth to be calculated. The $p_i(\omega)$ are further assumed to scale according to some well-defined range function $\eta(\vec{R}_i) \equiv \eta_i$, so that $p_i(\omega) = \eta_i^{-1} p(\omega/\eta_i)$, where $p(x)$ is also normalized. Thus the impurities produce a nuclear frequency disturbance which varies in a definite way with $\vec{R}$, but with a random distribution of amplitudes. This feature is designed to handle, in as general a fashion as possible, cases of impurity moments which are randomly oriented, whose magnetization is smeared out by random exchange fields, etc. Special cases will be discussed in Sec. III.

Under the above assumptions, then, the probability density (i.e., line shape) function $g(\omega)$ becomes[11]

$$g(\omega)\Delta\omega = \int_{-\Delta\omega/2}^{\Delta\omega/2} d\Omega \int d\Omega_1 \cdots \int d\Omega_N \delta\left(\sum_i \Omega_i - \omega - \Omega\right) \times \prod_{i=1}^{N}\left[(1-c)\delta(\Omega_i) + c\eta_i^{-1} p\left(\frac{\Omega_i}{\eta_i}\right)\right], \quad (1)$$

where the factor [ ] in Eq. (1) is the probability distribution of frequency shift at the origin due to site i and the product [in Eq. (1)] is taken over all N sites of the system (assumed large) excluding the origin. The occupation probability of any given site is c.

Expressing the δ function as

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} dt \exp\left[i\left(\sum_i \Omega_i - \omega - \Omega\right)t\right]$$

and performing the $\int d\Omega_i$ in Eq. (1) leads, as $\Delta\omega \to 0$, to

$$g(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t} \prod_{i=1}^{N}\left(1 - c + c \times \int_{-\infty}^{\infty} dx\, p(x) e^{ix\eta_i t}\right). \quad (2)$$

The product function in the integrand of Eq. (2) is therefore the "characteristic function" of the distribution or, in resonance terminology, the free-induction function $f(t)$ corresponding to line shape $g(\omega)$.

It is important to note that if the $p_i(\omega)$ contain discrete frequencies, then one may separate an arbitrary number of sites from this product function to be considered as generating "satellite" frequencies, with the remainder left to generate the breadths of the spectral components so produced. $f(t)$ is thus divided as follows:

$$f(t) = \prod_{i\ (\text{satellites})}\left(1 - c + c\int dx\, p(x)\, e^{ix\eta_i t}\right) \times \prod_{j\ (\text{breadth})}\left(1 - c + c\int dx\, p(x)\, e^{ix\eta_j t}\right), \quad (3)$$

with $\prod_i$ carried out over all sites considered to produce satellites and $\prod_j$ over the rest. All possible satellite frequencies with the correct statistical weights, normalized to unity, are generated by $\prod_i$ in Eq. (3). Further, it is clear that $\prod_j$ generates a breadth function that is the same for all satellites.

Dropping for the present the distinction between satellite sites and the rest, Eq. (3) may be reexpressed as

$$f(t) = \exp\left\{\sum_{n=1}^{\infty} \frac{(-1)^n c^n}{n(1-c)^n} \sum_{i=1}^{N}\left[1 - \left(\int dx\, p(x) e^{ix\eta_i t}\right)^n\right]\right\}. \quad (4)$$

Equation (4) is our principal result from which calculations in subsequent sections will be developed. The power series in $c/(1-c)$ enables one to calculate as many terms as required to determine $f(t)$ to a desired precision. This is then Fourier transformed to obtain $g(\omega)$. The result given by Cohen and Reif[13] follows from taking the leading term ($n=1$) in Eq. (4) and prescribing a δ function for $p(x)$.

Equation (4) is employed in later sections to make approximate calculations in very dilute systems, where an analytic form for the line shape is obtained, as well as for computer evaluations where the lattice sum $\sum_i$ is obtained to high precision. The power of this technique lies in the potential for calculating a frequency spectrum to arbitrary precision once $p(x)$ and the range function $\eta(\vec{R}_i)$ are specified.

III. CALCULATIONS OF DIPOLAR AND RKKY LINE SHAPES

We now consider in detail the NMR line shapes generated by magnetic impurities in solids through the RKKY and dipolar interactions. To fix ideas we consider the impurities to possess a spin $\vec{S}$ and assume a range function which includes both RKKY and dipolar interactions:

$$\eta_i = \frac{A\cos(2k_F R_i + \varphi) + B(1 - 3\cos^2\theta_i)}{R_i^3}, \quad (5)$$

where $R_i \equiv |\vec{R}_i|$ and θ_i is the angle between $\vec{R}_i$ and the applied field $\vec{H}_0$, which defines the z axis. η_i

is in units of rad/sec per unit spin. Next, we distinguish two cases.

(i) The motion of the spins $\vec{S}$ over their $2S+1$ sublevels is rapid compared with the NMR splittings and broadening they produce. Thus, the nuclei sense only the average moment $\langle S_{zi}\rangle$ at any site i.

(ii) In the opposite extreme, i.e., impurity-spin transitions slow compared with NMR linewidth, the nuclei sense the $2S+1$ separate impurity-spin orientations. For convenience we restrict ourselves to the case of a unique quantization axis throughout the crystal and therefore take

$$p(x)=\sum_{m_s} P(m_s)\,\delta(x-m_s)\,, \tag{6}$$

where $-S\le m_s\le S$ and $P(m_s)$ specifies a Boltzmann distribution of populations. Equation (6) applies either to very slowly relaxing electronic moments, or to an approximate treatment[12] of dilute like-spin line broadening. In the latter case, for $S=\frac{1}{2}$, we should retrieve the result obtained earlier by Anderson.

In Eq. (5) we have taken the asymptotic ($R_i\to\infty$) form[5] of the RKKY interaction in a nearly-free-electron metal. This should be more than adequate for the sake of line-shape assessment, as the first-few-neighbor shells contain relatively little statistical weight except at very high impurity concentrations.

Two types of calculated results are presented here. First, we describe approximate calculations valid in the limit of great dilution. These will subsequently be compared with machine computations in which the lattice sums of Eq. (4) are carried out explicitly for the first 400–600-neighbor shells, a continuum approximation being made beyond that point. Comparison of these two results, then, allows one to assess the effects of discreteness on the line shape, and establishes the concentration level at which the approximate (i.e., infinite-dilution) line shapes become valid.

A. Approximate calculations

Beginning with case (i), we set out to calculate the breadth function of Eq. (3) for very dilute impurities. The sum on i in Eq. (4) is therefore restricted to sites far enough from the origin that the lattice may be treated as a continuum, taking $\sum_i \to \rho\int d\vec{R}$, where ρ is the density of sites available to impurities. The $\int d\vec{R}$ is taken over all space outside a loosely defined cutoff radius $R_{\min}$, which marks the nearest distance at which the continuum approximation is considered valid. Further, the sum $\sum_i$ in Eq. (4) is averaged over the phase φ of the RKKY oscillations. At large R the change in R^{-3} over one RKKY period becomes negligible, whereupon the oscillation and decay variables in Eq. (5) may be separated. Integration over the RKKY period introduces, in effect, an average over φ. This may also be regarded as an assumption of infinite k_F. We also specify, at the outset, a sharp frequency distribution: $p(x)=\delta(x-\langle S_z\rangle)$. The general case of unspecified $p(x)$ is considered below.

On the above assumptions, then, the lattice sum in the nth term of $\ln f(t)$ [Eq. (4)] may be rewritten

$$\sum_i (1-e^{in\omega_i t})\cong\frac{\rho}{\pi}\int_0^{\pi} d\varphi\int d\Omega\int_{R_{\min}}^{\infty} R^2 dR\,(1-e^{in\omega(\vec{R})t})\,, \tag{7}$$

where $\omega_i=\langle S_z\rangle\eta_i$.

We note first that the imaginary part of (7), which generates the shift and antisymmetric part of the line, appears to diverge logarithmically as $R\to\infty$. In the RKKY case this divergence is only apparent as it is prevented by the $\cos(2k_F R+\varphi)$ factor [Eq. (5)]. In the dipolar case, however, there is a divergence which leads to a shift of the NMR line by the familiar "demagnetizing fields" from magneto-statics. We defer a detailed discussion of these matters to Sec. III B. For the present we simply drop the imaginary part of Eq. (7) and thus assume the line to be symmetric. This is not always obvious, particularly in the case of dipolar broadening by localized moments, where the local field distribution from each neighbor shell is asymmetric in the same sense. For such a case one has to rely on the superposition of many impurity fields at the same site to assure symmetry. The ultimate test of this assumption is, of course, the machine line-shape computation in Sec. III B.

Let us proceed with our approximate evaluation of the real part of Eq. (7) for case (i). In accord with assumptions spelled out above, $\omega(\vec{R})$ in Eq. (7) is written

$$\omega(\vec{R})=\langle S_z\rangle\frac{A\cos\varphi+B(1-3\cos^2\theta)}{R^3}\,.$$

Then, to carry out the radial integral in Eq. (7), one makes the change of variables

$$u=\langle S_z\rangle\,|\,A\cos\varphi+B(1-3\cos^2\theta)\,|\,nt/R^3,$$

leading to

$$\begin{aligned}\mathrm{Re}\sum_i (1-e^{in\omega_i t})\cong\frac{4\rho\langle S_z\rangle nt}{3}&\int_0^{\pi} d\varphi\\ &\times\int_0^1 dy\,|A\cos\varphi+B(1-3y^2)|\\ &\times\int_0^{u_{\max}}\frac{du}{u^2}\,(1-\cos u)\,,\end{aligned} \tag{8}$$

where $u_{\max}$ results from taking $R=R_{\min}$. We now define the dilute limit to be that where $u_{\max}$ is substantially infinite for the sake of evaluating $\int du$ in Eq. (8) for $n\ge 1$ and for, e.g., $t\ge\frac{1}{10}T_2^*$, where T_2^* is the inverse linewidth, to be obtained present-

ly. This condition also implies that the "zeros" of $u_{\max}$ in (φ, θ) space have negligible weight. In this limit we take

$$\int_0^{u_{\max}} du\,(1-\cos u)/u^2 \to \tfrac{1}{2}\pi$$

and Eq. (4) becomes

$$\ln[f_{\mathrm{dil}}(t)] = \frac{2\pi\rho\langle S_z\rangle t}{3}\sum_{n=1}^{\infty}(-1)^n\left(\frac{c}{1-c}\right)^n \times \int_0^{\pi} d\varphi \int_0^1 dy\left|A\cos\varphi + B(1-3y^2)\right| . \tag{9}$$

The subscript dil denotes dilute line shape. The sum on n may be immediately performed to give $-c$, whereupon $f_{\mathrm{dil}}(t)$ is seen to be an exponential decay with a decay constant linear in c. The corresponding line shape is a Lorentzian,

$$g_{\mathrm{dil}}(\omega) = T_2^*/\pi(1+\omega^2 T_2^{*2}) \ , \tag{10}$$

where

$$T_2^{*-1} = \frac{2\pi\rho c\langle S_z\rangle}{3}\int_0^{\pi} d\varphi \int_0^1 dy\left|A\cos\varphi + B(1-3y^2)\right| \tag{11}$$

for case (i). (Note we take $\langle S_z\rangle > 0$ throughout.)

The Lorentzian shape function found here also holds for arbitrary $p(x)$. However, in the latter case the power series in $c/(1-c)$ cannot be summed. We recast this series to give

$$f(t) = \exp\left[-\sum_{n=1}^{\infty}\frac{c^n}{n}\sum_i\left(1-\int_{-\infty}^{\infty} dx\,p(x)\,e^{it x\eta_i t}\right)^n\right], \tag{12}$$

and treat only the linear term in c. The advantage of Eq. (12) is that for a sharp distribution $p(x)$ all but the linear term vanish in the dilute limit. Treating this term in the same fashion as in the previous paragraph leads to a linewidth given, in general, by

$$T_2^{*-2} = \frac{2\pi\rho c\langle|x|\rangle_{\mathrm{av}}}{3}\int_0^{\pi} d\varphi \int_0^1 dy\left|A\cos\varphi + B(1-3y^2)\right| , \tag{13}$$

where $\langle|x|\rangle_{\mathrm{av}} = \int |x|\,p(x)\,dx$. In a [case (i)] situation where $p(x)$ is limited to essentially positive values of x, then, Eq. (11) is modified only to the extent of replacing $\langle S_z\rangle$ with $\langle S_z\rangle_{\mathrm{av}}$, where the average is over all spins in the system.

The upper limit of c for which Eqs. (10) and (11) are valid is determined by the assumption that the mean distance between impurities is large compared with $R_{\min}$ and with k_F^{-1}. For Eq. (12), one must also consider the effect of terms in c^2 and higher; it is clear from the series in Eq. (9) that such terms are quite small for $c \le 0.01$. We therefore focus our attention on the limits imposed by $R_{\min}$ and k_F. The condition for k_F^{-1} appears to be easily fulfilled, since k_F^{-1} is considerably smaller than the lattice constant in a typical metal. Effects of finite k_F are discussed further in connection with the results of Sec. III B. $R_{\min}$ appears to be a more serious problem, since one might guess that this radius encloses ~100 neighbor sites in the cubic metals. The associated concentration limit is then straightforwardly estimated from an evaluation of $\langle u_{\max}\rangle_{\mathrm{av}\,\theta,\varphi}$ for $n=1$, $t=\frac{1}{10}T_2$ using Eq. (11), giving

$$\langle u_{\max}\rangle_{\mathrm{av}\,\theta,\varphi} = (5\pi N_{\mathrm{av}})^{-1}, \tag{14}$$

where N_{av} is the average number of impurities found in a sphere of radius $R_{\min}$. Taking N_{av}/c ~100 sites, a generous estimate of the concentration where $u_{\max}$ is large would be [from Eq. (14)] $c \ll 0.01$. The results of Sec. III B bear this out as a reasonable estimate.

Both the Lorentzian character and the linear concentration dependence of the linewidth are seen to stem from the R^{-3} range dependence of η_i. In a more general case where $\eta(\vec{R})$ separates into an R^{-n} dependence times some function of angle and/or other variables, the sum in Eq. (7) will factor into $t^{3/n}$ times an infinite series in $c/(1-c)$. The line will, of course, have some shape other than Lorentzian for $n \neq 3$.

The case (ii) (slow-relaxation) linewidth follows straightforwardly from combining Eqs. (6) and (13), giving

$$T_2^* = \frac{2\pi\rho c\langle|S_z|\rangle}{3}\int_0^{\pi} d\varphi \int_0^1 dx \times\left|A\cos\varphi + B(1-3x^2)\right| , \tag{15}$$

where

$$\langle|S_z|\rangle = \sum_{m_s} P(m_s)\,|m_s| .$$

In the remainder of this section we consider the consequences of Eqs. (11) and (15) in several cases of interest.

(a) Dilute dipolar (and/or RKKY) line broadening, considering $S_z S_z'$ interactions only. This comes under case (ii) [Eqs. (6) and (15)]. Anderson[12] analyzed this case for purely dipolar broadening with $S=\frac{1}{2}$. This leads in Eq. (15) to $\langle|S_z|\rangle = \frac{1}{2}$ independent of polarization. For $A=0$ and $B=\frac{3}{2}\gamma^2\hbar$, Eq. (15) reduces to the result given by Abragam,[12] as it must. Interestingly, Eq. (15) enables us to generalize this result to higher spin values. For complete polarization $\langle|S_z|\rangle_{\mathrm{av}} \to S$, giving $T_2^{*-1} \propto S$, as expected. In the more usual case of high temperatures $[P(m_s) \to (2S+1)^{-1}]$, one finds $\langle|S_z|\rangle_{\mathrm{av}} = \frac{1}{4}(2S+1)$ (half-integral spin), $S(S+1)/(2S+1)$ (integral spin). Thus, large spin values are only half as effective in line broadening per unit moment as are spins of $\frac{1}{2}$. For half-integral spins this result can be expressed by

$$\frac{1}{T_2^*(S)} = \frac{2S+1}{2\,T_2^*(S=\frac{1}{2})} ,$$

where it is assumed that all parameters remain

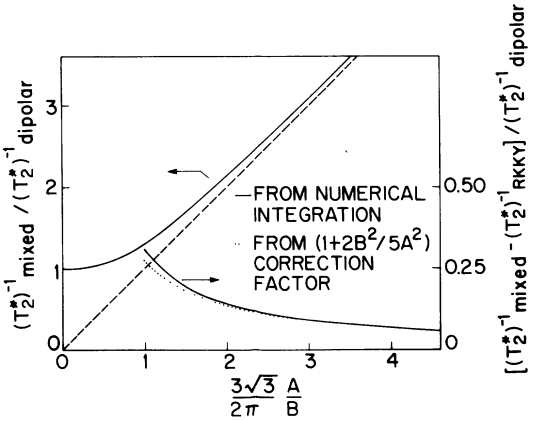

FIG. 1. Left-hand scale: half-width $(T_2^*)^{-1}_{\text{mixed}}$ for combined dipolar and RKKY coupling as a function of RKKY half-width, both in units of dipolar half-width (solid line). Dashed line—RKKY half-width for comparison. Right-hand scale: deviation of "mixed" half-width from RKKY value in units of dipolar half-width. Solid line—numerical integration of Eq. (11), dotted line—first nonvanishing correction term derived in text.

fixed except for the spin value. It is also interesting to note that the case (ii) linewidth is always within a factor of 2 or less of its maximum value $[\langle|S_z|\rangle_{\text{av}}]_{\max} = S$.

The remainder of the discussion is given in terms of case (i) but applies as well to case (ii) if we replace $\langle S_z\rangle_{\text{av}}$ with $\langle|S_z|\rangle_{\text{av}}$.

(b) Purely dipolar ($A=0$) or purely RKKY ($B=0$) coupling. For these cases the integrals in (11) may be carried out immediately to give

$$\frac{1}{(T_2^*)_{\text{dipolar}}} = \frac{8\pi^2\rho c}{9\sqrt{3}}|B|\langle S_z\rangle \tag{16}$$

and

$$\frac{1}{(T_2^*)_{\text{RKKY}}} = \frac{4\pi\rho c}{3}|A|\langle S_z\rangle, \tag{17}$$

the difference in coefficients reflecting simply the average magnitude of $1-3\cos^2\theta$ as opposed to that of $\cos\varphi$.

(c) The case encountered for magnetic impurities in metals is one of mixed RKKY and dipolar coupling. The double integral in (11) is not so simply evaluated for arbitrary ratio of A to B, so a machine evaluation was carried out. The results are plotted in Fig. 1. The composite linewidth (ordinate) is in units of the dipolar linewidth [Eq. (16)] while the abscissa, shown as the ratio A/B times a numerical factor, may also be regarded as the RKKY linewidth [Eq. (17)] in units of the dipolar linewidth. Deviation from the line of slope unity (dashed line) shows the extent to which the purely RKKY linewidth is modified by dipolar effects.

It is of interest to examine further the way in which these line-broadening mechanisms combine. For $B/A \ll 1$ this can be carried out with an approximate evaluation of (11) to obtain the first nonvanishing correction term to Eq. (17). The correction factor is easily found to be $(1+\frac{2}{5}(B/A)^2+\ldots)$. The correction term $\frac{2}{5}(B/A)^2$ is also plotted in Fig. 1 along with the deviation of the computed ("mixed") result from the RKKY linewidth. The lowest-order correction is seen to give a good account of the composite line-broadening effect for B/A values nearly as large as unity.

It is important to note that elementary arguments about combining linewidths do not work here. Simple addition of widths, which applies to Lorentzian broadening from independent sources, is obviously incorrect. Adding squares of linewidths yields a correction factor $(1+(\frac{1}{27}2\pi^2)(B/A)^2+\ldots)$, which has the correct functional form, but with a numerical coefficient in error by a factor of ~ 2. The point here is that these two sources of broadening interfere directly with one another, yielding a result which can only be found by detailed calculation.

B. Machine computations of line shapes

It remains to evaluate line shapes using the formulation of Sec. II for a variety of impurity concentrations in a specific lattice, under conditions where no further approximations of a serious nature are introduced. In this way, effects due to discreteness of the lattice and finite RKKY period can be assessed and, moreover, the assertion of a Lorentzian line shape as $c \to 0$ can be examined further. Calculations are carried out for the fcc lattice under case (i) of Sec. III A, using the range function of Eq. (5). We use the power-series expansion of Eq. (12), considering primarily the $n=1$ term with spot checks to determine the importance of the c^2 term. For simplicity the source distribution is taken as $p(x) = \delta(x - \langle S_z\rangle)$ as in Eqs. (7)–(11).

The primary quantity to be evaluated, then, is

$$f(t) = \exp\left(-c\sum_i (1-e^{i\omega_i t})\right) \tag{18}$$

for $0 \le t \le t_{\max} \sim 8T_2^*$, with $\omega_i = \langle S_z\rangle \eta_i$ as before. This function is then Fourier transformed to yield a line-shape curve. Our procedure is to take a discrete lattice sum over a spherical region of the crystal of radius R_0 such that $\omega_i t_{\max} < 1$ (i.e., $\omega_i T_2^* \ll 1$), for sites at the surface of the sphere. The contribution from sites outside the sphere is then estimated from a continuum approximation as follows. For the real part we take

$$\sum_i (1-\cos\omega_i t) \cong \tfrac{1}{2}\rho t^2 \int_{|\vec{R}|\ge R_0} d\vec{R}\,\langle\omega^2(\vec{R})\rangle_{\text{av}\,\varphi}, \tag{19}$$

where the brackets $\langle\ \rangle_{av\,\varphi}$ indicate an average over the RKKY phase φ. For the imaginary part we take a linear approximation to $\sin\omega_i t$:

$$\sum_i \sin\omega_i t \cong tp \int_{|\vec{R}|\geq R_0} d\vec{R}\,\langle\omega(\vec{R})\rangle_{av\,\varphi}\,. \qquad (20)$$

Taking $\omega(R)$ from Eq. (5) we immediately see from Eq. (20) that the RKKY contribution vanishes. The dipolar part produces a combined demagnetizing and Lorentz correction given by $c\sum_i \sin\omega_i t \cong \gamma t(\frac{4}{3}\pi - D)M$, where γ is the nuclear gyromagnetic ratio, D the demagnetizing factor of the sample, and M the volume magnetization due to the impurities. This effect is simply a frequency shift

$$\Delta\omega = (\tfrac{4}{3}\pi - D)\,\gamma M, \qquad (21)$$

which is to be added to that found from the discrete contribution to $f(t)$.

The Fourier transform of $f(t)$ is obtained for frequencies $-5/T_2^* \leq \omega \leq 5/T_2^*$ by means of a 256-point Simpson's-rule evaluation over the range $0 \leq t \leq 8T_2$. This procedure yielded an accuracy of $\sim 3\times10^{-4}$ with an exponential input function. In evaluating $f(t)$ the frequencies ω_i were truncated at $\pm 20/T_2^*$, since frequencies outside this range are not handled well by the Fourier-transform procedure.

We now turn to a discussion of specific results.

1. RKKY case

The case of pure RKKY coupling was evaluated first, since only the distribution of spherical shells of neighbors is needed. This distribution was obtained with a machine sorting technique for the first 600-neighbor shells (~87 000 sites), giving agreement on the innermost shells with published work.[15] The free-electron value for k_F was adopted here, assuming one electron per site in the fcc lattice. Thus we have $k_F a = (12\pi^2)^{1/3}$, where a is the fcc lattice constant. The RKKY phase was taken to be $\varphi = 1.06\pi$, corresponding roughly to one's expectation for *Cu*Mn.[16]

Computer line shapes for a series of concentrations ranging from 0.01 to 1% are given in Fig. 2, where the discrete sum in Eq. (18) was taken over 600-neighbor shells ($R_0 \cong 17a$). The frequency scale is in units of the dilute-limit linewidth [Eq. (17)], which is $(1/T_2^*)_{RKKY} = 16\pi cA\langle S_z\rangle/3a^3$ for the fcc lattice. Note that the absolute frequency scale changes by a factor of 100 over the stated range of c. The solid curves are Lorentzians with the dilute-limit linewidth, but with shifts adjusted to fit the computed results.

The dilute-limit shape and width are in excellent accord with the 0.01% results, which deviate by less than 1% of the peak value over the $\pm 5/T_2^*$ frequency range. The width agrees to better than 0.5%. Deviations from Lorentzian shape appear

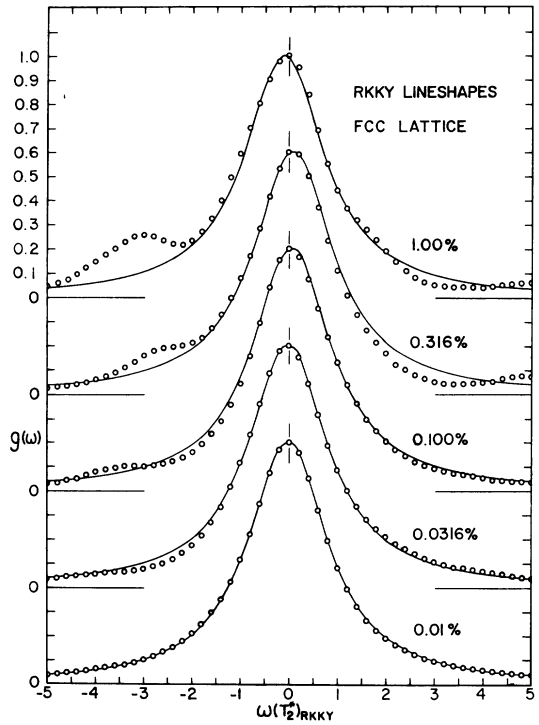

FIG. 2. Computer evaluation of RKKY line shapes for fcc lattice with RKKY phase $\varphi = 1.06\pi$, normalized to peak values of unity (circles). Solid lines are Lorentzians with dilute-limit RKKY half-width [Eq. (17)]. Concentration ranges from $c = 0.01\%$ up to 1.0%.

for $c > 0.01\%$, but the width remains in good accord up through 1.00%. The results of Fig. 2 are a strong indication that the dilute-limit line shape and width [Eqs. (10) and (11)] are asymptotically correct. However, it is not possible to say whether the deviations from Lorentzian shape at higher concentrations are due to finite RKKY period or to discreteness of the lattice.

The shifts in Fig. 2 are generally less than $0.1/T_2^*$ and fluctuate from one side to the other. It would clearly require extraordinarily careful work to make an experimental interpretation of the shifts. Satellite lines are easily identified by making a histogram of ω_i for the first few neighbor shells. The large one at -3 for $c = 1.00\%$ is, for example, due to third neighbors.

Two checks were performed to validate our procedures in obtaining the results of Fig. 2. First, the boundary between the discrete and continuous regions [R_0 in Eqs. (19) and (20)] was changed for the $c = 0.01\%$ case, for which the greatest sensitivity is expected. Shrinking the discrete region from 600- to 400-neighbor shells was found to produce changes $< 0.1\%$ of the computed spectrum. On the other hand, the $c = 1.00\%$ spectrum would be most sensitive to the neglect of $n > 1$ terms in Eq.

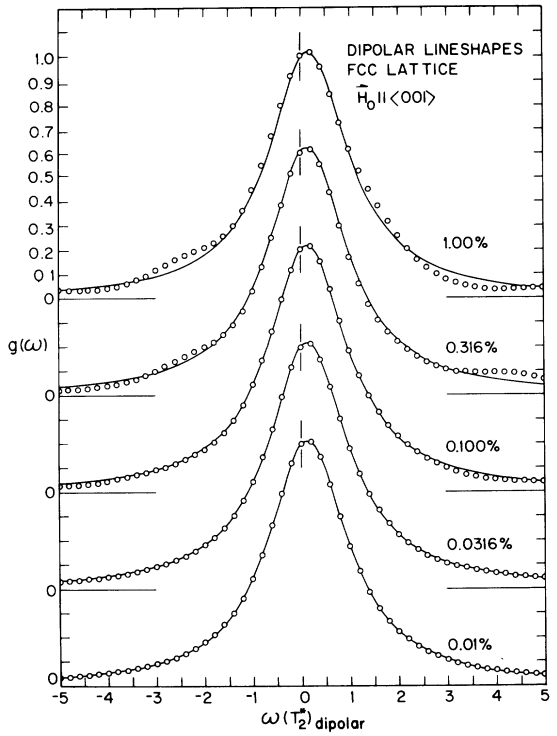

FIG. 3. Computer evaluation of dipolar line shapes for fcc lattice, normalized to peak value of unity (circles). Solid lines are Lorentzians with dilute-limit half-widths [Eq. (16)]. Concentration ranges from 0.01% up to 1.0%.

(12). There, inclusion of the $n=2$ term was found to alter the results by ~0.1% near the center and at most by a few percent in the wings. Finally, altering the RKKY phase for the 0.01% curve produced changes less than 1% of the peak value.

2. *Dipolar case*

The inclusion of dipolar couplings requires considerable elaboration of the procedure, since one must now tabulate the values of $1-3\cos^2\theta_i$ within a given shell of neighbors. Such a tabulation was carried out assuming the field to lie along ⟨001⟩ in the fcc lattice for the first 400-neighbor shells ($R_0 \cong 14a$). This includes ~45 000 sites and ~3000 distinct sets of $[(1-3\cos^2\theta_i),\ R_i]$ parameters. For this case one finds $\omega_i t_{\max} \sim 2.8$ at the surface of the discrete region, for which Eq. (19) would not seem sufficiently accurate. Evaluation of the t^4 term, however, shows it to be, at worst, only ~7% of the t^2 term, so that the error produced in $f(t)$ by Eq. (19) is $\lesssim 0.2\%$. A further check was performed by reducing the discrete sum from 400-neighbor shells to 300 for $c=0.01\%$. This produced errors of less than 0.5% in the computed spectrum.

The dipolar results are given in Fig. 3, again for $0.01\% \le c \le 1.00\%$. The solid curves are, as before, Lorentzians with the dilute-limit linewidth, which is $(1/T_2^*)_{\text{dipolar}} = 32\pi^2 Bc\langle S_z\rangle/9\sqrt{3}\,a^3$ for the fcc lattice. There are two noticeable differences between these and the results of Fig. 2. First, the dilute-limit theory is valid at considerably higher concentrations in the dipolar case. This is attributed to the smoothing effect of the $1-3\cos^2\theta$ variation over a given shell in the dipolar case and/or the contribution of finite k_F to the irregularities found in the higher-concentration results of Fig. 2. In any case, the smoothness observed at $c=1.0\%$ in Fig. 3 is quite remarkable in view of the criterion of Eq. (14).

Second, all the dipolar lines are noticeably shifted by $\Delta\omega \sim 0.15/T_2^*$ in a positive direction. This shift arises from the discrete sum only, since the continuum part of the shift [Eq. (21)] is not included in Fig. 3. The origin of this shift may be sought in the general expression

$$\int_{-\infty}^{\infty} \omega g(\omega)\, d\omega = \left.\frac{df}{dt}\right|_{t=0} = c\sum_i \omega_i \,.$$

What is striking here is that this sum vanishes in a cubic system, a point which has been explicitly checked with the array of $[(1-3\cos^2\theta_i),\ R_i]$ parameters used here.[17] The shifts in Fig. 3 can therefore arise only through satellites well removed to the left of the line.

It is interesting to compare the shift [Eq. (21)] with the dipolar width. For the flat-disk geometry ($D=4\pi$), one obtains $\Delta\omega(T_2^*)_{\text{dipolar}} = -1/\pi$, giving a maximum shift still considerably less than the half-width at half-height. This result applies only to case (i). In case (ii) $\Delta\omega(T_2^*)_{\text{dipolar}}$ will in gener-

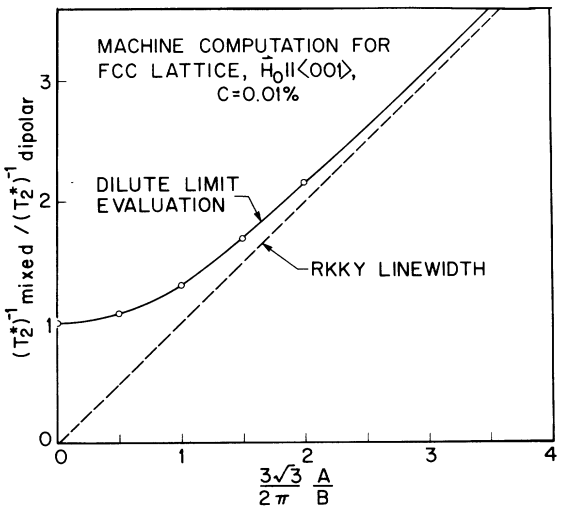

FIG. 4. Half-widths of computer-evaluated line shapes with combined dipolar and RKKY coupling for $c=0.01\%$ (circles), plotted as in Fig. 1 with dilute-limit half-width from Eq. (11) (solid line).

al be much smaller.

It is finally noted that the assumption of line-shape symmetry for the dilute limit in Sec. III A is thoroughly justified by the results of Fig. 3.

3. *Mixed RKKY and dipolar coupling*

Computed line shapes were also obtained for several B/A ratios at $c = 0.01\%$ in an effort to corroborate the calculations in Fig. 1. The resulting line shapes, which are not shown in full, were of the same quality as in Figs. 2 and 3 at $c = 0.01\%$. The half-widths are plotted in Fig. 4 along with the dilute-limit curve from Eq. (11) (Fig. 1), where the agreement is seen to be excellent.

C. Comparison with previous results

The calculated Lorentzian half-width for the RKKY case is compared with the results of earlier work in Table I. The fcc lattice is assumed here, and the broadening coefficient W is defined by $(T_2^*)^{-1}_{\mathrm{RKKY}} = WA\langle S_z\rangle c/a^3$. The earliest work[8,9] assuming essentially a single-impurity broadening effect is seen to err rather widely, but to bracket the present result. The more recent work of Mizuno[6] differs by only $\sim -4\%$ from our value, a discrepancy which is probably due to performing the successive-convolution calculation in a sphere of limited radius. Alloul[7] has obtained values even closer to our $W = \frac{16}{3}\pi$ by this technique. It is gratifying that these two rather different computational approaches yield essentially the same results.

TABLE I. Comparison of broadening factors W from previous theories with the present result.

W	Source
11.2π	Behringer[a]
2.8π	Chapman and Seymour[b]
5.13π	Mizuno[c]
5.33π	Present work

[a]Reference 8.
[b]Reference 9.
[c]Reference 6.

IV. IMPURITY-DAMPED RKKY OSCILLATIONS

Several years ago it was demonstrated by Heeger, Klein, and Tu[14] that the addition of Al impurities to dilute *Cu*Mn caused the Mn-induced RKKY broadening of the Cu NMR lines to diminish. This effect was attributed to damping of the RKKY oscillations through electron scattering by the Al impurities. A rough theory for this line narrowing effect was given,[14] leading to an exponential decrease of Cu NMR linewidth with λ_{sp}^{-1}, where λ_{sp} is an effective mean free path for the damping of spin oscillations. On the reasonable assumption that $\lambda_{sp}^{-1} \propto c'$, the aluminum concentration, a qualitative accord with the experimental results was found.

As a further illustration of the methods of Secs. II and III, we present calculations of line shapes and widths for the case of damped RKKY oscillations Following Ref. 14, we take [with $p(x) = \delta(x - \langle S_z\rangle)$ in Eq. (12)]

$$\omega_i = \eta_i\langle S_z\rangle = \frac{A\langle S_z\rangle \cos(2k_F R_i + \varphi)\, e^{-R_i/\lambda_{sp}}}{R_i^3}, \qquad (22)$$

where for simplicity the relatively minor dipolar effect is neglected—its importance will be assessed later. de Gennes[18] has shown that an equation of this form is certainly not valid at short distances. However, for the asymptotic $R_i \gg a$ region that concerns us here, Eq. (22) is probably a reasonable *ansatz* if one thinks in terms of elementary resistivity theory. Unless otherwise noted, the discussion here refers to the results of Ref. 14.

Before proceeding with the calculated results, it is interesting to note that as a by-product of our present calculation we shall be able to estimate the self-damping effect that magnetic impurities have upon their own RKKY oscillations when they are present in a host metal at some concentration c. Thus we shall develop a simple check on whether the range function $\eta(\vec{R}_i)$ introduced in Sec. II can be considered independent of the impurity concentration.

The bulk of the calculations for this case were made with the dilute-limit theory of Sec. III A. Recalling the discussion there, we can conclude immediately from the altered R dependence of Eq. (22) that the resulting line shape will not be Lorentzian, as was reported. However, the difference may be difficult to detect experimentally. No simple line shape function is found to emerge here. With the assumptions of Sec. III A one can only say that the dilute-limit impurity line shape is the Fourier transform of

$$f(t) = \exp\left[-\left(\frac{2t}{\pi T_2^*}\right)\int_0^\infty \frac{du}{u^2}\sin^2\!\left(u\exp[-(t/\pi u N_\lambda T_2^*)^{1/3}]\right)\right], \qquad (23)$$

where $T_2^{*-1} = \frac{4}{3}\pi\rho cA$ is the dilute-limit undamped RKKY value, and $N_\lambda = \frac{4}{3}\pi c\rho\lambda_{sp}^3$ is the average number of magnetic impurities contained in a sphere of radius λ_{sp}. Equation (23) returns to the undamped limit [Eq. (11), $B \to 0$] as $N_\lambda \to \infty$, as it must. One can see that the exponential factor in the argument of $\sin^2$ in Eq. (23) has the effect of diminishing the integrand for small u and thus the decay rate of $f(t)$. It is difficult to say more about $f(t)$ without machine evaluations, except that an appreciable effect should be present when $N_\lambda \sim 1$.

Computed line shapes have been obtained with Eq. (23) for a series of N_λ values giving equal increments of λ_{sp}^{-1} and thus of aluminum concentration c' in the $(Cu\text{-}Al)$: Mn experiments. The minimum value of N_λ considered is unity, for which

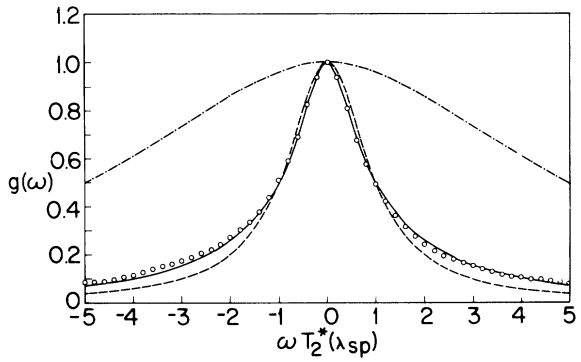

FIG. 5. Computer evaluation of exponentially damped RKKY line shape for fcc lattice for $c = 0.01\%$ with $N_\lambda = 1 (\lambda_{sp} = 8.4a)$ (circles). Solid line is dilute-limit line shape evaluated from Eq. (23), whose half-width is taken to be $1/T_2^*(\lambda_{sp})$. Dashed line is Lorentzian with same half-width for comparison. Dash-dot line is undamped RKKY line profile under the same conditions.

case a discrete lattice-sum line shape evaluation was also made for $c = 0.01\%$ using Eq. (22) with the $n = 1$ term of Eq. (12). The discrete and dilute-limit line-shape curves for $N_\lambda = 1$ are both plotted in Fig. 5, where the over-all agreement is less good than for $c = 0.01\%$ in Figs. 2 and 3, but generally satisfactory. Also shown in Fig. 5 are a Lorentzian curve of the same half-width, which reveals a noticeable deviation from Lorentzian behavior for the computed line shapes, and the Lorentzian curve of the undamped RKKY line at this concentration, which calibrates the line-narrowing effect of the RKKY damping to be in this case a factor of about 5.

Behavior of the computed half-width as a function of $N_\lambda^{-1/3} (\propto \lambda_{sp}^{-1})$ is shown in Fig. 6. Interestingly, the line narrowing is a very nearly exponential function of λ_{sp}^{-1} as found experimentally, a fact which appears to be accidental in the present treatment. The behavior of Fig. 6 is quite accurately represented by

$$\frac{T_2^*(\infty)}{T_2^*(\lambda_{sp})} = e^{-1.59 N_\lambda^{-1/3}} . \tag{24}$$

As an initial assessment of the experimental results, we apply Eq. (24) to the observed decrease in linewidth plotted in Ref. 14, yielding $\lambda_{sp} = 74a$ (a is the Cu lattice constant) for 1 at.% Al doping. This value is almost twice the $\lambda_{sp} \sim 40a$ deduced by the authors in an approximate analysis. Further, Eq. (24) may be seen to *underestimate* λ_{sp} since it applies to the half-width, whereas the peak-to-peak derivative width (which was actually measured) decreases somewhat more rapidly. A close examination of Fig. 5 shows that the latter quantity is slightly smaller, relative to the half-width, than for a Lorentzian curve. This has the effect of increasing the estimated λ_{sp}.

We therefore find an effective mean free path λ_{sp} rather closer to the resistivity value $\lambda_r \sim 140a$ quoted in Ref. 14 (for 1 at.% Al) than in the analysis given there. Other data indicate, however, that λ_r may be even larger. Vassel[19] reports for this system a residual resistivity of $\Delta\rho = 0.8\ \mu\Omega$ cm/at.% Al. Interpreted on a free-electron model with one electron/atom, this gives $\lambda_r \sim 230a$. It appears then that λ_r and λ_{sp} for this system are significantly different.

As the RKKY width decreases in an experiment such as this, the dipolar width contribution becomes increasingly important since it is not sensitive to disorder. For the case at hand (i.e., *Cu*Mn) with $J_{sd} \sim 1$ eV, A is about an order of magnitude greater than B [see Eqs. (6) and (11)], so that even after a reduction by a factor of ~ 3 in the line-narrowing experiments, the RKKY width is still several times the dipolar one. From Fig. 1, then, we conclude that dipolar effects remain essentially negligible.

Let us now apply the results of Fig. 6 and Eq. (24) to the phenomenon of self-damping, i.e., to the damping of RKKY oscillations by the impurities which produce them. To do this we use electrical-resistivity data to estimate the concentration at which Eq. (24) predicts a 10% narrowing effect. For the self-damping case, Eq. (24) becomes

$$\frac{T_2^*(\infty)}{T_2^*(\lambda_{sp})} = \exp[-1.61(\rho c)^{2/3} \sigma_{sp} n] , \tag{25}$$

where σ_{sp} is the effective scattering cross section and n the number of conduction electrons/atom. Equation (25) expresses the fact that, as the concentration is increased, the RKKY damping effect grows more rapidly than the Lorentzian linewidth.

From residual resistivity measurements[19,20] on

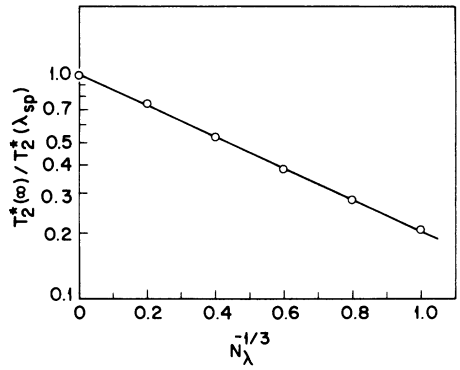

FIG. 6. Half-widths for exponentially damped RKKY case in units of undamped half-width $[T_2^*(\infty)^{-1}]$ as a function of $N_\lambda^{-1/3} \propto \lambda_{sp}^{-1}$. Solid line is exponential decay $\exp(-1.59\ N_\lambda^{-1/3})$ for comparison.

*Cu*Mn ($\Delta\rho \sim 4\ \mu\Omega$ cm/at.% Mn) we obtain the resistivity scattering cross section $\sigma_r = 0.54a^2$. Adopting this as an estimate of σ_{sp} and taking $n = 1$ in Eq. (25), we obtain a 10% narrowing effect for $c = 0.02$. Further, if σ_{sp} for *Cu*Mn is several times larger than σ_r, as appears to be the case for *Cu*Al, then the estimated c for 10% narrowing could drop by nearly an order of magnitude. In any case it is clear that self-damping effects are potentially important even for concentrations less than 1 at.%.

We conclude this section by noting that the unique range-function assumption of Sec. II may become invalid in cases of relatively high concentration. The onset of this effect is characterized by a decrease of the slope of linewidth versus magnetic impurity concentration. In cases where magnetoresistive effects are important one may also find that impurity linewidth contribution fails to track the magnetization curve. Finally, the results of the elementary model of Ref. 14 are essentially confirmed except for a numerical factor of the order of 2.

V. CONCLUSIONS AND DISCUSSION

From a well-established formulation of the problem of randomly distributed impurities, we have developed a technique for calculating the field or frequency distribution at any point in a lattice. Application here has been limited to the standard cases of RKKY and dipolar couplings. Nonetheless, it is clear that this is a method of considerable generality, so that line shapes and widths can be evaluated for any situation for which a range function can be written down. It has been used, for example, by Lang *et al.*[21] to estimate linewidth contributions from Co pairs in *Cu*Co.

For the RKKY and dipolar couplings our results show the dilute line to be Lorentzian and give the linewidth law for combinations of these two interactions, which cannot be derived by simple arguments. The Lorentzian shape for dilute dipole-dipole broadening has been derived some time ago for spin $\frac{1}{2}$ by statistical arguments[12] and by means of the method of moments.[22] The present work generalizes this result to higher spin values and shows that it does not simply scale with S. We show further that the dilute line shape is Lorentzian for any coupling which varies basically as R^{-3}, regardless of additional modulating factors which vary with angle, spin orientation, etc. We also conclude that interactions which do *not* vary as R^{-3} will, by the same reasoning, *not* generate lines of Lorentzian shape.

It is to be emphasized that the line shapes calculated here are strictly valid only in the absence of other sources of line broadening. One can incorporate other (independent) sources of *static* broadening by a straightforward convolution procedure. Taking account of homogeneous (i.e., dynamic spin-spin) broadening is a rather more involved question, since the inhomogeneous broadening will detune neighboring spins to a degree which depends on the relative amounts of homogeneous and inhomogeneous broadening present. For strong inhomogeneous broadening then, one need only take account of the static spin-spin coupling.

As an example of dipolar broadening, we cite the study of ^{19}F NMR in impurity-doped antiferromagnetic MnF_2 by Butler *et al.*[23] There, by doping of Zn^{++} into MnF_2, one obtains a random distribution of "holes" in the magnetic lattice which act as impurity moments of magnitude $g\mu_B S$ for the sake of the dipolar line-broadening effect. Using Eq. (13) with $A = 0$, $B = 2\gamma\mu_B$, and $p(x) = \frac{1}{2}[\delta(x - S) + \delta(x + S)]$, we obtain Eq. (16) with $\langle S_z \rangle = S$ and $\rho = 2/a^2c$ (a^2c is the MnF_2 unit cell volume). Numerical evaluation yields $1/\gamma T_2^* = 60$ G/at.% Zn, in good agreement with the measurements.

Another example of interest (see Sec. IV) is the exponentially modulated RKKY interaction (due to resistivity damping) first treated by Heeger *et al.*[14] This leads to a narrowing of the purely RKKY-broadened line, and a distortion of the Lorentzian shape which is noticeable in the calculations, but which may be difficult to detect experimentally. This effect may be divided into damping due to the magnetic impurities which also generate the RKKY broadening (self-damping) and damping due to the resistivity of the host. In the former case the line-narrowing effect increases initially as $c^{2/3}$ (c is the magnetic impurity concentration) and becomes appreciable for magnetic impurity resistivity of the order of a few $\mu\Omega$ cm/at.% impurity. at $c \sim 1$ at.%. The host damping effect varies, in contrast, as $\rho_{\text{host}} c^{-1/3}$. It becomes important, for example, in a metal having the resistivity of Cu at 0 °C (1.7 $\mu\Omega$ cm) for $c \gtrsim 0.01$ at.%. It is clear that one must be careful to avoid these effects in RKKY linewidth studies.

One might also apply the methodology we have presented here to the exchange-field distributions which occur in RKKY exchange-coupled magnetic impurity systems occasionally referred to as "spin glasses." Evaluation of such distributions would help to determine whether the properties of these systems can be understood with the RKKY model and to what extent these properties scale with concentration in the manner proposed by Souletie and Tournier.[24]

The application of our results to NMR linewidths in dilute alloys such as *Cu*Mn, *Ag*Mn, etc., is left for a future publication, since a detailed discussion of these matters goes beyond the intended scope of the present paper.

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