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Microscopic Inhomogeneous Broadening and Nuclear Spin-Spin Interactions

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We study here the effects that random inhomogeneities have both on the nuclear spin-spin interaction via virtual spin-wave excitations in magnetically ordered systems [the Suhl-Nakamura (S-N) interaction] and on dipolar interactions. Two models are proposed to explain the experimental observation that the nuclear transverse relaxation rates ($1/T_2$) often are smaller than predicted by the S-N or dipolar theories for the perfect crystal, and that the spin-echo envelope decays are exponential in time rather than Gaussian. For both models, the method of moments is employed, and it is shown that the transformation from Gaussian to cutoff Lorentzian behavior may be characterized by the behavior of the quantity $(M_4)_{\mathrm{in}}/(M_2)_{\mathrm{in}}^2$. Assuming the magnitude of the inhomogeneous broadening to be the same, a proportionately greater reduction occurs in $(M_2)_{\mathrm{in}}^{\mathrm{S-N}}$ than in $(M_2)_{\mathrm{in}}^{\mathrm{dip}}$ when the range of the S-N interaction is large (i.e., $H_A/H_E \ll 1$). The inhomogeneous model as applied to the dipolar interaction compares favorably with Portis's spectral diffusion theory. The limitations of the applicability of the model theories to comparison with experiment are considered. Finally, a number of serious errors in the S-N theory, as applied to $\mathrm{MnF_2}$, are corrected.

I. INTRODUCTION

THE sources of the dynamic broadening of nuclear-magnetic-resonance (NMR) line profiles in solids are either spin-spin or spin-lattice interactions. It is an unfortunate circumstance that, often as not, the observed resonances are statically broadened as a result of inhomogeneities which cause the frequency for resonance to vary from point to point in the crystal. Such inhomogeneous broadening, if large, not only masks the homogeneous broadening from the dynamic mechanisms but, in the case of the spin-spin interaction may actually reduce its effectiveness. It is this problem which is the concern of the present work and is of particular interest in regard to ferromagnets and antiferromagnets, where inhomogeneous broadening is the rule rather than the exception.

As an important source of the broadening of the NMR in ferromagnets and antiferromagnets Suhl[1] and Nakamura (S-N)[2] independently proposed an indirect exchange coupling between nuclear spins in these systems. The mechanism proceeds as follows: a nuclear spin I_i at the site i creates a virtual spin wave via the transverse part of the hyperfine interaction ($AI_i^+S_i^-$); this virtual spin wave is then reabsorbed by a nuclear spin at the site j ($AI_j^-S_j^+$), giving an effective coupling between the two nuclei of the form

$$\mathcal{H}_{\mathrm{S\text{-}N}} = \sum_{i\neq j} V_{ij} I_i^+ I_j^- , \tag{1.1}$$

where $V_{ij} = (A^2/2Jz) f(\mathbf{r}_{ij})$ the quantity J is the interion electronic exchange coupling between the z nearest-neighbor spins S and $f(\mathbf{r}_{ij})$ is the S-N range function. For those magnetic solids in which the nuclei in question are isotopically abundant the coupling $\mathcal{H}_{\mathrm{S\text{-}N}}$ yields a resonance linewidth $(\Delta E)_{\mathrm{S\text{-}N}} \simeq CA^2I/2Jz$ with 1 C 20 depending on the ratio of exchange to anisotropy energies. The magnetic dipolar interaction $\mathcal{H}_{\mathrm{dip}}$ between nuclei leads to linewidth $(\Delta E)_{\mathrm{dip}} \simeq \mu_n^2/Ia_0^3$ with μ_n the nuclear moment and a_0 the nearest-neighbor distance. It frequently happens in magnetic crystals (e.g., Co^{59} in metallic Co and Mn^{55} in $\mathrm{MnF_2}$) that $A^2I/2Jz \gg \mu_n^2/Ia_0^3$ from which one concludes $\mathcal{H}_{\mathrm{S\text{-}N}}$ should be the primary source of line broadening.

We shall concern ourselves with the effects that microscopic inhomogeneities have on the S-N and dipolar interactions. Both from the viewpoint of motivation and to make contact with the extensive experimental and theoretical work that has been performed on $\mathrm{MnF_2}$ (and related crystals), we focus our attention on this particular antiferromagnet. However, the models that are proposed are of sufficient generality as to be immediately applicable to other systems.

The original calculation by Nakamura[2] of the F^{19} resonance line shape in $\mathrm{MnF_2}$ appeared to be in excellent agreement with earlier steady-state continuous-wave (cw) measurements, in which it was observed[3] that the line profile was Gaussian with a width of 14 Oe. The theoretical prediction of an approximately Gaussian line with a 13.6 Oe width was thought to be strong confirmation of the S-N theory. However, subsequent transient experiments[4] on the identical crystal gave results that seemingly contradicted both theory and the cw experiment; namely, spin echoes were observed,

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showing that resonance is inhomogeneously broadened, and the decay of the echo envelope was exponential in time indicating that the *homogeneous* line profile was Lorentzian. Most distressing, however, was the fact that the inferred homogeneous linewidth was an order of magnitude smaller than was predicted originally. We have reexamined Nakamura's theory, and it now appears that the F^{19} S-N interaction is much smaller than was previously given. Nevertheless, similar discrepancies between earlier cw experiments and subsequent spin-echo studies have been noted.[5] In fact there exists no direct experimental confirmation of the S-N theory from transient measurements of the homogeneous line profile.

Now it is well known that if inhomogeneities are present—and in particular random *microscopic*[6] inhomogeneities—the steady state and transient experiments no longer measure the same properties as they would in an ideal homogeneous system. Only in the latter case would we expect the cw linewidth to be identical with the inverse of the transverse relaxation time T_2. The cw experiments suffer from being sensitive to inhomogeneities, both microscopic and macroscopic, often to the point where the linewidth has little to do with spin-spin interactions of any kind. The transient experiments, on the other hand, *do* measure the dynamic effects alone, that is, either spin-spin or spin-lattice interactions, and therefore are to be preferred in comparing experiment with theory.

We suggest that these general properties, of homogeneous linewidths being much smaller than the inhomogeneous ones and the echo decay envelope being exponential rather than Gaussian, are consistent with a model of microscopic inhomogeneous broadening of the resonance-frequency (or local-magnetic-field) distribution. Such inhomogeneities may separate (detune) the resonant frequencies of a pair of nuclear spins to such an extent as to strongly inhibit mutual spin flips; i.e., in the presence of severe detuning the interaction described by Eq. (1.1) or the corresponding dipolar Hamiltonian will not conserve nuclear Zeeman energy. The interaction between spins will, of course, induce transitions, but its effect will be appreciable only if the interaction strength is at least of the order of the *difference* in Zeeman energies of the two nuclei. The reduction in the number of allowed transitions due to detuning would lead, in particular, to a longer transverse relaxation time.

In order to discuss these effects more quantitatively it is convenient to employ the usual moment description of the line profile, $g(\omega)$. A complete description is contained in the specification of all moments,[7] where the nth moment is defined by

$$M_n=\int_{-\infty}^{\infty}(\omega-\omega_0)^n g(\omega)d\omega\,, \tag{1.2}$$

with ω_0 the central resonance frequency, and $g(\omega)$ normalized to unity: $\int_{-\infty}^{\infty} g(\omega)d\omega=1$. Although in practice it is usually only feasible to compute the lower-order moments ($n\leq 4$) these are often sufficient to characterize the gross line shape, especially if the line is symmetric about ω_0, so that the odd moments vanish. In this case a fair indication of the line profile is given by the ratio M_4/M_2^2, which is identically three for a Gaussian line and tends to infinity for a Lorentzian one. The detuning via microscopic inhomogeneity that we have proposed clearly reduces all moments; only those pairs of spins with resonance frequencies close enough to communicate are reflected in the spin-echo envelope decay, and the monotonic decrease in probability of finding such pairs, as $|\omega-\omega_0|$ increases, enhances the central region relative to the wings. However, the higher moments are more sensitive than are the lower ones to any weight in the wings. In the absence of inhomogeneities the resonance line is broadened by spin-spin interactions, with the wings of the line representing the effects of the strong (short-range) components of the interaction. The corresponding absorption processes are relatively less susceptible to detuning than are those involving weakly interacting spins and the higher moments are thereby reduced less than the lower ones. In particular, as the detuning increases, the calculated ratio M_4/M_2^2 increases, resulting in an apparent line narrowing and a gradual transformation of the Gaussian line shape to a Lorentzian one. Of course, the measured cw NMR is inhomogeneously broadened at the same time that T_2 is increased.

In Sec. II we review briefly the S-N theory as it applies to this problem. Only the antiferromagnet is considered because meaningful comparisons between experiment and theory have been made only for this case. We have seen above that the form of the interaction at small nuclear separations will be required. We give the results of numerical calculations of the interaction between neighboring nuclei for a realistic range of ratios of anisotropy to exchange fields H_A/H_E, and we compare the numbers with the frequently quoted long-range asymptotic expression. For $H_A/H_E \leq 0.03$ [as is the case in MnF_2 (0.016), but not in FeF_2 (0.32)], the asymptotic form is found to be sufficiently accurate for further calculations. The corrections to Nakamura's expressions for the Mn^{55} and F^{19} linewidths and correct expressions for M_4 are also given.

In Sec. III we present two model calculations exhibiting the effects of detuning discussed qualitatively in this Introduction. In the first model we assume the spatial fluctuations in the field to be so large that

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[5] Examples of these are the Co^{59} NMR in Co metal and CoF_2.

[6] We define microscopic in this context to mean that there exists no correlation between the resonance frequency of a particular spin and its position in the lattice.

[7] See, for example, A. Abragam, *The Principles of Nuclear Resonance* (Oxford University Press, London, 1961).

the affected nuclear spins have their resonance frequencies well removed from the main NMR line. Such a condition is tantamount to a simple dilution of the resonant nuclear spins. The second model considers the more realistic situation of an inhomogeneously broadened line of width $\Delta\omega$ large compared to the S-N interaction strength V_{ij} between any pair (ij) of spins. To this we apply the rough criterion that any two spins, i and j, are considered capable of interacting if, and only if, the difference in their resonance frequencies is less than V_{ij} (the relevance of this criterion is explored in Appendix C). The latter model is also applied to the dipolar interaction in the presence of inhomogeneities for the simple cubic lattice for arbitrary nuclear spin magnitude I. It is shown to agree semiquantitatively with Portis's spin-$\frac{1}{2}$ spectral diffusion theory.[8] Finally, comparison between experiment and theory is made for representative cases where the spin-spin interaction is larger than, and where it is smaller than, the inhomogeneous broadening.

II. SUHL-NAKAMURA INTERACTION IN ANTIFERROMAGNETS

A. Form of the Interaction

We follow here Nakamura's calculations,[2] which take as a model a simple two sublattice antiferromagnet, with all nearest neighbors (nn) of an "up" spin on the "down" sublattice, and vice versa. Exchange is described by the single nn exchange integral J and single-ion uniaxial anisotropy by a constant K, with the unperturbed electron-spin Hamiltonian

$$\mathcal{H}_0=2J\sum_{j,\delta}\mathbf{S}_j\cdot\mathbf{S}_{j+\delta}-\tfrac{1}{2}K[\sum_j (S_j^z)^2+\sum_k (S_k^z)^2], \quad (2.1)$$

where j is to be summed over the up sublattice, k over the down sublattice, and δ over nn vectors. By the usual simple (unrenormalized) spin-wave approximation this Hamiltonian is diagonalized in the subspace of the perfectly aligned Néel state and the manifold of single-spin deviation states, with spin-wave energies

$$\omega_q=2JSz[(1+d^2)^2-\gamma_q^2]^{1/2}. \quad (2.2)$$

Here z is the number of nearest neighbors, and[9]

$$d^2=H_A/H_E=(1-1/2S)K/2Jz;$$

$$\gamma_q=\frac{1}{z}\sum_{\delta}^{\mathrm{nn}} e^{i\mathbf{q}\cdot\boldsymbol{\delta}}. \quad (2.3)$$

We first consider the case in which the nuclear spins and electronic spins occupy the same sites. Furthermore, we assume a given nuclear spin I_n has a hyperfine interaction only with its own electronic spin S_n. The coupling of these spin waves to the nuclear spin system via the hyperfine interaction is taken as a perturbation

$$\mathcal{H}'=A\sum_n [I_n^zS_n^z+\tfrac{1}{2}(I_n^+S_n^-+I_n^-S_n^+)], \quad (2.4)$$

where n is to be summed over both sublattices. At low temperatures the z component is almost ineffective in polarizing the electron spin, and its effects are ignored. The transverse part of $\mathcal{H}'$ couples the ground state of $\mathcal{H}_0$ to states with a single-spin excitation, giving a second-order ground-state energy shift which can be represented[2] by an effective nuclear-spin Hamiltonian

$$\mathcal{H}_{\mathrm{eff}}=\tfrac{1}{2}D\sum_n (I_n^z)^2-\tfrac{1}{2}\sum_{j\neq j'} B_{jj'}I_j^+I_{j'}^- -\tfrac{1}{2}\sum_{k\neq k'} B_{kk'}I_k^+I_{k'}^- -\sum_{j,k} C_{jk}(I_j^+I_k^-+I_j^-I_k^+). \quad (2.5)$$

The first term represents a self-energy shift of the nth nuclear spin, due to emission and reabsorption of a virtual magnon. It is quadrupolar in form and will not contribute to the dephasing of the transverse spin components in the transient experiments. The last term ($\sim C_{jk}$) represents spin-flip processes in which the energy transfer is large, since the local fields are in opposite directions at j and k. This nonsecular term leads to satellite resonance lines rather than to broadening of the central line, and we ignore it. We are primarily interested in the term representing mutual nuclear spin flips on a single sublattice, characterized by the range function

$$B_{nn'}=\frac{2A^2JzS^2}{N}(1+d^2)\sum_q\frac{\cos\mathbf{q}\cdot(\mathbf{n}-\mathbf{n}')}{\omega_q^2} \equiv\frac{A^2}{2Jz}f(\mathbf{n}-\mathbf{n}'). \quad (2.6)$$

An approximate expression for the sum over the Brillouin zone was obtained in the original papers[1,2] by taking advantage of the fact that for large $|\mathbf{r}|\equiv|\mathbf{n}-\mathbf{n}'|$ and small anisotropy (and therefore small gap in the spin-wave excitation spectrum ω_q) the sum is dominated by the small q contribution. Keeping only the q^2 term in the small q expansion of ω_q we then obtain the usual asymptotic form

$$B(\mathbf{r})\approx[A^2(1+d^2)/8\pi\alpha Jz](e^{-\kappa r}/r)$$

or

$$f(r)=(1/4\pi\alpha)(e^{-\kappa r}/r)[1+d^2], \quad (2.7)$$

where α is a geometrical factor ($=\frac{1}{4}$ for the bcc lattice), and the decay constant $\kappa=d[(2+d^2)/\alpha]^{1/2}\approx d(2/\alpha)^{1/2}$. The assumption of the dominance of small values of q in the sum (2.6) is valid only for r sufficiently large for the oscillations of the numerator to suppress large q contributions ($r\geq$ lattice constant). We reemphasize, however, that it also requires small anisotropy ($d\ll 1$)

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[8] A. M. Portis, Phys. Rev. **104**, 584 (1956).

[9] The factor $(1-1/2s)$ in the definition of d^2 is missing in Ref. 2, but this, in effect, just renormalizes the gap, Δ, there. It does correctly include the vanishing of anisotropy terms in the energy when $S=\frac{1}{2}$.

so that the spin-wave energy gap will be small and the low q contributions will be appreciable in spite of the limited-phase space volume there. For larger anisotropies it is useful to compute the expansion of $f(\mathbf{r})$ as a power series in $(1+d^2)^{-1}$

$$f(\mathbf{r})=\frac{1}{(2\pi)^3}\frac{1}{1+d^2}\sum_{n=0}^{\infty}\int_{\mathrm{BZ}} d^3q\left(\frac{\gamma_q}{1+d^2}\right)^{2n}\cos\mathbf{q}\cdot\mathbf{r}. \quad (2.8)$$

By the orthogonality relations on $e^{i\mathbf{q}\cdot\mathbf{r}}$ integrated over the Brillouin zone (BZ), we see that the first nonvanishing term in the sum over n is the one for which γ_q^{2n} contains $e^{\pm i\mathbf{q}\cdot\mathbf{r}}$ (which value of n, of course, increases with r). Furthermore, all terms in the sum are positive so that $f(\mathbf{r})>0$ at all *lattice points* in any lattice. This is *not* true if the definition of $f(\mathbf{r})$ is extended to all $\mathbf{r}$; it will then be found to oscillate on a scale of the lattice constant. One must therefore be wary of approximating sums over lattice sites by integrals when the summand involves $f(\mathbf{r})$.

For a bcc crystal, where $\gamma_q=\cos\frac{1}{2}k_x\cos\frac{1}{2}k_y\cos\frac{1}{2}k_z$, the result of the integration in Eq. (2.8) can be written simply. The range function $f(\mathbf{r})$ is anisotropic [in contrast to Eq. (2.7)]; in particular,

$$f(\mathbf{r})=\sum_{n=l}^{\infty}\left(\frac{1}{4}\right)^{3n}\binom{2n}{n}^{2}\binom{2n}{l+n}\left(\frac{1}{1+d^2}\right)^{2n+1}, \quad \text{for} \quad \mathbf{r}=(l,0,0), \quad (2.9\text{a})$$

$$f(\mathbf{r})=\sum_{n=l}^{\infty}\left(\frac{1}{4}\right)^{3n}\binom{2n}{l+n}^{3}\left(\frac{1}{1+d^2}\right)^{2n+1}, \quad \text{for} \quad \mathbf{r}=(l,l,l), \quad (2.9\text{b})$$

where we have used the standard notation for binomial coefficients. For sufficiently large d^2 only the term $n=l$ contributes appreciably to these sums. Then the ratio of $f(\mathbf{r})$ at successive points is approximately

$$\frac{f(l+1,0,0)}{f(l,0,0)}\approx\frac{1}{16}\left(\frac{2l+1}{l+1}\right)^2\left(\frac{1}{1+d^2}\right)^2, \qquad \frac{f(l+1,l+1,l+1)}{f(l,l,l)}\approx\frac{1}{64}\left(\frac{1}{1+d^2}\right)^2, \quad (2.10)$$

whereas the asymptotic form gives

$$\frac{f(l+1,0,0)}{f(l,0,0)}=\frac{l}{l+1}\exp[-2d(2+d^2)^{1/2}], \qquad \frac{f(l+1,l+1,l+1)}{f(l,l,l)}=\frac{l}{l+1}\exp[-2d(6+3d^2)^{1/2}]. \quad (2.11)$$

In this (somewhat unrealistic) limit of $d\gg1$, it is clear that the actual range function falls off much more slowly than the asymptotic form indicates. Since the asymptotic expression becomes infinite at the origin, the actual and asymptotic curves must cross.

The behavior of $rf(r)$ for realistic values of d is shown in Fig. 1; the value $\sqrt{2}d=0.179$ is appropriate for $\mathrm{MnF_2}$. The predicted crossing of asymptotic and actual curves as d increases is clearly seen. The fact that the real and asymptotic forms closely approach each other for small values of d is also shown.

The theory also predicts an indirect exchange coupling between the nuclei of nominally nonmagnetic ions which have transferred hyperfine interactions with two or more neighboring magnetic spins.

In particular it was thought that this was essential for understanding the $\mathrm{F^{19}}$ NMR linewidth in $\mathrm{MnF_2}$. Unfortunately, the theory as given is in serious error and, as it turns out, the $\mathrm{F^{19}}$ S-N interaction is of negligible importance as compared with the dipolar interaction. The reasoning behind this is of sufficient interest to warrant giving some of the details below.

In these crystals each F atom has three magnetic nearest neighbors, all in a {110} plane, as shown in Fig. 2. These may be two "up" spins and one "down" or vice versa, but only two $\mathrm{F^{19}}$ nuclei with the same environment can interact (to second order in the hyperfine coupling), for only then can energy be conserved in a mutual nuclear spin flip. With the coordinates of such a second $\mathrm{F^{19}}$ nucleus and its neighbors denoted by the same symbols as in Fig. 2, but with primes added, a calculation of the same type described above for nuclei of magnetic atoms gives for an effective Hamiltonian that couples the $\mathrm{F^{19}}$ nuclei

$$\mathcal{H}_{\mathrm{eff}}=-\tfrac{1}{2}\sum_{j>j'}D_{jj'}(I_j^+I_{j'}^-+I_j^-I_{j'}^+) \quad (2.12)$$

with

$$D_{jj'}=\frac{2J\tilde{A}^2S}{N}\sum_q\frac{\cos\mathbf{q}\cdot(\mathbf{j}_3-\mathbf{j}_3')}{\omega_q^2}\{[3+2\cos\mathbf{q}\cdot(\boldsymbol{\rho}_1-\boldsymbol{\rho}_2)]\times(1+d^2)-2(\cos\mathbf{q}\cdot\boldsymbol{\rho}_1+\cos\mathbf{q}\cdot\boldsymbol{\rho}_2)\gamma_q\}$$
$$\equiv(\tilde{A}^2/2Jz)\tilde{f}(\mathbf{j}-\mathbf{j}'), \quad (2.13)$$

where $\tilde{A}$ is the transferred hyperfine coupling constant[10]

$$\mathcal{H}_{\mathrm{hf}}=\tilde{A}\sum_j\mathbf{I}_j\cdot(\mathbf{S}_{j1}+\mathbf{S}_{j2}+\mathbf{S}_{j3}) \quad (2.14)$$

and $\tilde{f}(\mathbf{j}-\mathbf{j}')$ is the corresponding normalized range function, whose exact dependence on $\mathbf{r}=\mathbf{j}-\mathbf{j}'$ will not concern us for the present.

Equation (2.13) is equivalent to Eq. (23a) in Ref. (2), but when the latter was transcribed [in Eq. (24a)] for further use, an error was made in the relative sign of the two terms in { }, leading to gross numerical errors. The physical significance of this relative sign is most easily seen in the long wavelength limit, where all the cosine factors in Eq. (2.13), as well as $\gamma_{q'}$ go to unity.

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[10] To simplify the calculation we assume all the transferred hyperfine interaction to be equal and isotropic. A negligible error is introduced by this approximation as far as the $\mathrm{F^{19}}$ NMR in $\mathrm{MnF_2}$ is concerned.

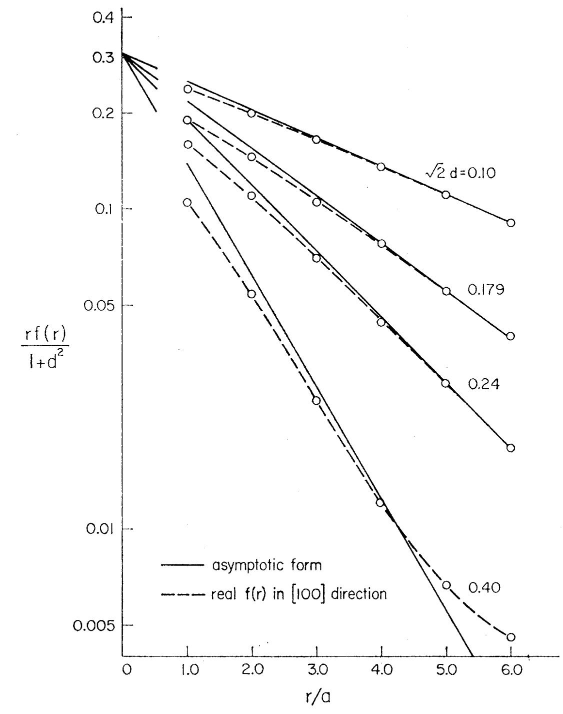

FIG. 1. The spatial variation of the S-N range function $f(r)$ in a bcc antiferromagnet in the [100] direction. The logarithm of the dimensionless quantity $rf(r)/(1+d^2)$ is plotted versus r/a. Both the long wavelength asymptotic form for $f(r)$ (see Eq. 2.7) and the exact result are given for various values of $\sqrt{2}\,d$, with the value $\sqrt{2}\,d=0.179$ being appropriate to MnF_2.

In coupling to the $q=0$ spin wave the F^{19} nucleus feels a transverse hyperfine field in Eq. (2.14) from the "down" Mn spin, S_{j3}, which is 180° out of phase with the field from the two "up" spins, S_{j1} and S_{j2}, and the effective coupling strength is therefore reduced. Mathematically, the corresponding pieces of the matrix element of $\mathcal{H}_{\mathrm{hf}}$ between the ground and one spin-wave intermediate states have opposite signs. All this is, of course, equally true for the reabsorption of the virtual spin wave by the second nucleus. The cross terms in the second-order matrix element, appearing as the second term in { } in Eq. (2.13), must enter with an over-all negative sign, substantially reducing the coupling in the $q=0$ limit. In fact, the net effect is of the order of the coupling to a single spin, instead of to 3. Because this calculation is second order in $\mathcal{H}_{\mathrm{hf}}$, the { } in Eq. (2.13) goes to unity instead of 9 as $q\rightarrow 0$. More importantly, this factor of 9 tends to be *squared* in the calculation of the second moment, as will be discussed in more detail in Sec. II B.

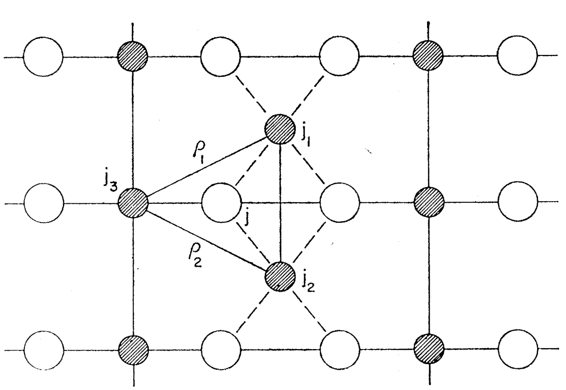

FIG. 2. The ion positions in the (110) plane in the MnF_2 lattice with the shaded and open circles representing the Mn^{2+} and F^- ions, respectively. The three nn Mn^{2+} spins to the jth F^- ion consist of two (j_1,j_2) on the up (down) sublattice and one (j_2) on the down (up) sublattice (after Ref. 2).

B. Moment Calculation

With the form of the effective interaction between nuclear spins established we can employ the techniques originally introduced by Van Vleck[11] to calculate the moments of the line profile resulting from that interaction. We make the usual approximations of total nuclear spin disorder (infinite nuclear-spin temperature) and zero electron-spin temperature; it has been shown[12] that corrections are small at temperatures $T\ll T_N$ in all materials for which frequency pulling effects are unimportant. Then, the formalism relates the moments to traces over nested commutators of the total x component of spin I_x with the interaction Hamiltonian

$$M_2=\frac{\mathrm{Tr}\{[\mathcal{H}',I_x]^2\}}{\mathrm{Tr}I_x^2}, \tag{2.15a}$$

$$M_4=\frac{\mathrm{Tr}\{[\mathcal{H}',(\mathcal{H}',I_x)]^2\}}{\mathrm{Tr}I_x^2}. \tag{2.15b}$$

But the operator form of the S-N interaction, $I_n^+I_{n'}^- + I_n^-I_{n'}^+$, is just that of the transverse components of the secular part of the dipole-dipole interaction, which has been treated in detail.[7,11] Those results can then be brought over directly,[2,13] and we have

$$M_2=\tfrac{1}{3}I(I+1)\sum_{j'}B_{jj'}^2, \tag{2.16a}$$

$$M_4=\left[\frac{I(I+1)}{3}\right]^2\left[5(\sum_{j'}B_{jj'}^2)^2-\frac{2}{N}\sum_{j',j''}B_{jj'}^2B_{j'j''}B_{j''j} +3\sum_{j'}B_{jj'}^4\left(1-\frac{1}{2I(I+1)}\right)\right], \tag{2.16b}$$

or

$$M_4=\left[\frac{I(I+1)}{3}\right]^2\left[3(\sum_{j'}B_{jj'}^2)^2 +\frac{1}{N}\sum_{j\neq j'\neq j''\neq j}B_{jj'}^2(B_{jj''}-B_{j''j'})^2 +\sum_{j'}B_{jj}{}'^4\left(5-\frac{3}{2I(I+1)}\right)\right]. \tag{2.16c}$$

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[11] J. H. Van Vleck, Phys. Rev. **74**, 1158 (1948).

[12] P. Pincus, Phys. Rev. **131**, 1530 (1963).

[13] L. B. Vatova, Fiz. Tverd. Tela **7**, 2133 (1965) [English transl.: Soviet Phys.—Solid State **7**, 1717 (1966)].

It must be remembered that $B_{jj'}$ is defined only for $j\neq j'$. Thus, for example,

$$\sum_{j'} B_{jj'}{}^2 \sim \sum_{q,q'} f(q,q') \sum_{j\neq j'} \cos\mathbf{q}\cdot(\mathbf{j}-\mathbf{j}') \cos\mathbf{q}'\cdot(\mathbf{j}-\mathbf{j}')$$
$$=\sum_{qq'} (N\delta_{qq'}-1) f(q,q'). \quad (2.17)$$

In the expression given by Nakamura for M_2, appropriate to the Mn^{55} resonance in $\mathrm{MnF_2}$, this last "self-energy" term $(j=j')$ was not explicitly subtracted. The corrected expression is

$$M_2(\mathrm{Mn})=\tfrac{1}{3}I(I+1)(A^2/2Jz)^2[f-f^2(0)], \quad (2.18)$$

where

$$f=\frac{1}{N}\sum_q [(1+d^2)^2-\gamma_q{}^2]^{-2}, \quad (2.19)$$

and $f(r)$ is the range function defined above (Eq. 2.6). For the Mn nuclear spins in $\mathrm{MnF_2}$, Nakamura has calculated $f=2.65$ and $f(0)=1.28$; thus the correction due to the $f(0)$ term reduces his value of M_2 by a factor of 2.6, to give

$$M_2(\mathrm{Mn})=1.02\times\tfrac{1}{3}I(I+1)(A^2/2Jz)^2.$$

The second moment appropriate to the F^{19} resonance in $\mathrm{MnF_2}$ requires additional corrections to be made. With $\boldsymbol{\varrho}_1$ and $\boldsymbol{\varrho}_2$ defined in Fig. 2 we find

$$M_2(F)=\tfrac{2}{3}I(I+1)\left(\frac{\tilde{A}}{2Jz}\right)^2\{f'-\tfrac{1}{2}[4-(1+5d^2+4d^4)f(0)$$
$$+2(1+d^2)f(\boldsymbol{\varrho}_1-\boldsymbol{\varrho}_2)]^2\}, \quad (2.20)$$

$$f'=\frac{1}{N}\sum_q [(1+d^2)^2-\gamma_q{}^2]^{-2}\{[3+2\cos q\cdot(\boldsymbol{\varrho}_1-\boldsymbol{\varrho}_2)]$$
$$\times(1+d^2)-2\gamma_q(\cos\mathbf{q}\cdot\boldsymbol{\varrho}_1+\cos\mathbf{q}\cdot\boldsymbol{\varrho}_2)\}^2. \quad (2.21)$$

It is to be noted that Eq. (2.21) and Eq. (24a) of Ref. 2 differ in the sign of the second term in the { }. [See discussion following Eq. (2.14)]. This has as a consequence, the fact that the long-wavelength asymptotic behavior of f and that of f' are now identical (i.e., $f=f'=1/\pi d\sqrt{2}$) rather than differing by a factor of 81 as had been thought, previously (see Eq. 31 of Ref. 2). The sums contained in Eqs. (2.19) and (2.21) are evaluated in Appendix A.

The fourth moment resulting from the S-N interaction has been investigated in Ref. 13 (with self-energy terms correctly excluded). It is indicated there that for the magnetic nuclei in a system for which anisotropy is small enough to make possible the long-wavelength approximation to the $\omega(q)$ factors in sums over $\mathbf{q}$ (e.g., Mn in $\mathrm{MnF_2}$) $M_4/M_2{}^2\approx 6$. In Appendix B we show this estimate to be in error and that in fact $3<M_4/M_2{}^2<5$ for *all* values of H_A/H_E. Nevertheless, we would still expect no appreciable departure from a Gaussian-shaped line profile. Thus, the theory as it has been applied so far, without regard to microscopic inhomogeneities and to dipolar effects, is inadequate to explain the observations of the transient experiments. Before exploring these effects we note that one might also be tempted to make a more direct contact with experiment by using the actual spin-wave spectrum as determined by neutron diffraction. However, cancellation from various parts of the BZ, as evidenced in the usual orthogonality relations in sums over $\mathbf{q}$, plays a sufficiently important role to require knowledge of the dispersion relation over the whole zone, rather than only in the few symmetry directions that have been explored.

III. MODELS OF INHOMOGENEOUS BROADENING

The calculations of Sec. II apply to the perfectly homogeneous crystal. Real crystals, particularly ferromagnets or antiferromagnets, are subject to a number of imperfections which may lead to sizable inhomogeneities in the static local field seen by the nuclei. For instance, if a nonmagnetic impurity (e.g., Zn^{2+}) replaces a Mn^{2+} ion in $\mathrm{MnF_2}$ the $5\mu_B$ deficiency generates a local dipolar field. A random distribution of such spin impurities would lead to a *static* inhomogeneous broadening[14] of both the F^{19} and Mn^{55} NMR which would increase with increasing concentration of the specific impurity. The F^{19} NMR is also sensitive to strains and dislocations because of the overlap and/or transfer origin to its hyperfine interaction while the Mn^{55} NMR, having a hyperfine interaction of core polarization origin, is not. The former fact appears to be the major source of the cw linewidth of the F^{19} resonance even in nominally stoichiometric $\mathrm{MnF_2}$, $\mathrm{CoF_2}$ and $\mathrm{FeF_2}$.

For a given concentration of impurities, the broadening of the cw line profile and the reduction of the transverse relaxation rate that results depend upon three factors: (i) the distribution of impurities, (ii) the magnitude of the local fields created by the impurities relative to those already present in the perfect crystal, and (iii) the range of the nuclear spin-spin interaction(s). As regards the first, we will assume the inhomogeneous broadening to result from a completely random distribution of imperfections and to be microscopic in nature. The example of $\mathrm{MnF_2}$ will serve to demonstrate the importance of the second factor. A relatively good crystal of $\mathrm{MnF_2}$ still has a sufficient number of imperfections (vacancies, impurities, strains. etc.) such as to cause a static inhomogeneous broadening of, say 10–20 G, in what would be the line profile of either the F^{19} or Mn^{55} NMR in the absence of either S-N or dipole-dipole interactions. However, the calculations of the preceding section lead to widths of the order of 2 and 300 G for the F^{19} and Mn^{55} resonances, respectively,

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[14] For a dilute concentration this would not result in a microscopic inhomogeneous broadening.

resulting from H_{dip} and $H_{\text{S-N}}$. Clearly, then, we may expect the inhomogeneous broadening to have a pronounced effect on the F^{19} resonance properties and but little effect on the Mn^{55} resonance; in the former instance, energy conservation in a neutral spin flip would be difficult to achieve, while in the latter case it would not.

The third factor enters in a more subtle, yet important, manner. It is usually the case in discussing the dipolar interaction and the effects that inhomogeneities might have on the resonance properties to compare the perfect crystal M_2 (or rather the linewidth, which is proportional to $M_2^{1/2}$) with the inhomogeneous broadening, rather than to examine the strength of the interaction at some specific separation relative to the latter quantity. There is good reason for this. The dipolar interaction falls off so rapidly with distance that the primary contribution to

$$M_2{}^d \propto \sum_{i\neq j} f(\theta_{ij}) r_{ij}{}^{-6}$$

comes from nearest neighbors. Hence, the strength of the interaction at nearest neighbors and $M_2^{1/2}$ are comparable in size. The situation as pertains to the S-N interaction is quite different, particularly in the case where the anisotropy field H_A is much smaller than the exchange field H_E. In this latter instance we have shown that the asymptotic form for the range function $F(r) \propto r^{-1} e^{-\kappa r}$ is still good at small distances, that is, $r < 1/\kappa$. If, for discussion purposes, we replace sums by integrals then

$$M_2{}^{\text{S-N}} \simeq \left(\frac{A^2}{2Jz}\right)^2 \int_a^\infty e^{-2\kappa r}\, dr,$$

so that a substantial contribution to $M_2{}^{\text{S-N}}$ arises from nuclei separated by as much as $1/(2\kappa)$. However, nuclei this far distant from each other have an interaction which is $2\kappa a$ *smaller* than is the interaction of nn; hence, it is easier for them to be "detuned" by a given inhomogeneity than would be the case for nn. Thus, if we considered the hypothetical case of a crystal in which $M_2{}^{\text{S-N}} = M_2{}^{\text{dip}}$ and assume $1/\kappa \gg a$, we would expect a given inhomogeneity to be more effective in reducing the S-N interaction than it would be in reducing the dipolar interaction, so that $(M_2{}^{\text{S-N}})_{\text{in}} < (M_2{}^{\text{dip}})_{\text{in}}$. We now consider two models which treat the effects of inhomogeneities on the S-N and dipolar second and fourth moments.

A. Dilute Crystal

A given nucleus can lose transverse spin memory via the S-N interaction only with other nuclei whose resonance frequencies (or local fields) are sufficiently close to its own to allow for an energy conserving mutual spin flip. In the presence of the strong static inhomogeneities discussed above such nuclei are in low abundance and may be considered approximately as a dilute concentration of mutually interacting spins. The simplest model just replaces the actual system by a dilute concentration, c, of nuclear spins in identical local fields. The interaction of dilute concentrations of dipoles has been examined in detail,[7,15] and we follow those treatments here, simply substituting the S-N form of the interaction for the dipole-dipole one. The expressions (2.16a) and (2.16b) for the second and fourth moments M_2 and M_4 may be taken over directly to this model, with the simple replacement of sums over all lattice sites by sums over the occupied sites only. If we assume the inhomogeneities to be random (or, effectively a random distribution of interacting spins) we may make the replacement

$$\sum_{j(\text{occ})} \rightarrow c \sum_j \tag{3.1}$$

with the final sum taken over all lattice sites. Then the dilute crystal second moment becomes simply

$$M_2{}^c = cM_2, \tag{3.2}$$

where M_2 is the second moment for the homogeneous (or 100% concentration) crystal, Eq. (2.16a).

The calculation of the fourth moment proceeds in a similar fashion. We find for the dilute crystal

$$M_4{}^c = (5c^2) M_2{}^2 - \frac{2c^2}{N} \sum_{i\neq j\neq k\neq i} V_{ij}{}^2 V_{jk} V_{ki} + \left[8 - \frac{3}{2I(I+1)} - 5c\right] c \sum_j V_{ij}{}^4, \tag{3.3}$$

where $V_{ij} = B_{ij}$ for the metal nuclei in the transition metal fluorides and $V_{ij} = D_{ij}$ for the F^{19} nuclei [see Eqs. (2.6) and (2.13)]. For high concentrations ($c \rightarrow 1$) the last term is small and was therefore neglected in the $c=1$ calculation of M_4 in Ref. 12. However, at sufficiently low concentration this term will dominate, as the probability ($\sim c^2$) of finding two nuclei to interact with a given one decreases sufficiently below the probability ($\sim c$) for finding one such nucleus.

As a particular application of the above, we consider the case of the Mn^{55} resonance in MnF_2; a calculation of the ratio $M_4{}^c/(M_2{}^c)^2$ gives

$$M_4{}^c/(M_2{}^c)^2 \simeq R + 0.12/c, \quad (Mn^{55}, \text{S-N}), \tag{3.4}$$

where R is a quantity $3 < R < 5$ (see Appendix B). Since it is necessary that this ratio be of order 10 or more for the resonance to approach a Lorentzian shape, we see that c would have to be 3% or less. The value of $1/T_2 = \hbar\delta$ that would be expected using a cutoff Lorentzian is obtained from[7]

$$\delta = \tfrac{1}{6}\pi\sqrt{3}(M_2{}^2/M_4)^{1/2} M_2{}^{1/2}. \tag{3.5}$$

It follows then that if 3% or fewer of the nuclei are

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[15] C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).

interacting either by reason of genuine isotopic dilutions (in the perfect crystal) or by reason of inhomogeneous broadening (in the imperfect but dense crystal) the line profile would tend more towards a Lorentzian shape than a Gaussian one. In point of fact, for the Mn^{55} NMR in MnF_2, since it is required that the inhomogeneous linewidth $\Delta \gg M_2^{1/2}$ for the model to be applicable, an inhomogeneous broadening of considerably more than 10^3 G would be necessary. This is not the case in actual crystals.

For the F^{19} NMR in both MnF_2 and FeF_2 the dipolar interaction exceeds the S-N interaction. We may therefore directly apply the dilute dipolar model[7,15] to these resonances. Equation (3.2) applies equally well to both the S-N and dipolar interactions and in place of Eq. (3.4) we have[7]

$$M_4^c/(M_2^c)^2 \simeq 2+0.2/c\,, \quad (F^{19}, \text{dip})\,, \qquad (3.6)$$

which would require $c<2\%$ for $M_4/(M_2^c)^2$ to exceed 10. The F^{19} NMR in FeF_2 is found to be inhomogeneously broadened with $\Delta \simeq 10$ Oe and $M_2^{1/2}=2.1$ Oe from F^{19} dipolar interactions alone. Since the echo-decay envelope is more exponential than Gaussian, let us assume c to be no larger than 2% and estimate δ. Using Eq. (3.5), we find $\delta=0.6$ Oe, which is to be compared with the observed value $1/T_2 \simeq 1$ Oe. This model is perhaps too crude to attach much significance to any numerical results. Nevertheless, we feel this simplest of all models gives some physical insight into the detuning process. We pursue this line of investigation further by way of a more sophisticated model.

B. Inhomogeneous Line

1. *S-N Interaction*

Suppose that we have an inhomogeneously broadened NMR line described by the normalized shape function $g(\omega)$, which is to be determined by a random distribution of local fields. Suppose further that the width of this line $\Delta \approx g^{-1}(\omega_0)$, where ω_0 is the central frequency, is larger than the S-N width $(M_2)^{1/2}$, so that the steady-state line is essentially independent of the S-N interaction. Any pair of nuclear spins (i,j), then, has associated with it a difference in resonance frequencies, $\omega_{ij}=\omega_i-\omega_j$ with a distribution determined by $g(\omega)$. Qualitatively, then, we may expect a certain amount of detuning to exist which will lead to a reduction in the ability of the S-N interaction to dephase the nuclear spins, and as Δ increases, that part of T_2 arising from the S-N interaction also increases. The parameter determining the effectiveness of this detuning to inhibit flip-flops for a given pair is $\rho_{ij}=|V_{ij}/\hbar\omega_{ij}|$. If $\rho_{ij} \gg 1$ we may consider the spins to be tuned; on the other hand, for $\rho_{ij} \ll 1$ the energy conservation requirement rules out mutual spin flips. In order to simplify the computations we shall consider that for pairs of nuclei for which $\rho_{ij} \geq 1$ the S-N perturbation is secular and for those for which $\rho_{ij}<1$ complete detuning exists. Although this is a rather crude approximation to the smoothly varying behavior between the two limiting cases, we expect that it will give correct order-of-magnitude results. The nature of this approximation for two spins $\frac{1}{2}$ is considered in Appendix C.

As in the dilute crystal model the general expressions for M_2 and M_4 [Eqs. (2.16a) and (2.16b)] need be modified only by restricting the sums over interacting pairs (i,j)—in this case to those for which $|\hbar\omega_{ij}| \leq V_{ij}$. Thus,

$$\sum_j V_{ij}^2 \rightarrow \sum_j V_{ij}^2 g(\omega_i)\omega_{ij}^*\,, \qquad (3.7)$$

where ω_{ij}^* is the maximum value of ω_{ij} that satisfies the criterion $\rho_{ij} \geq 1$. The quantity $g(\omega_i)\omega_{ij}^*$ is the probability that a given nuclear spin (j) is within the frequency range $\pm\omega_{ij}^*$ of ω_i. From the definition of ρ_{ij} we see that in our model $\hbar\omega_{ij}^*=|v_{ij}|$. The second moment, $(M_2)_{\text{in}}$, is then expressed as

$$(M_2^i)_{\text{in}}=\tfrac{1}{3}I(I+1)\hbar^{-1}g(\omega)\sum_j V_{ij}^2|V_{ij}|$$
$$=M_2\hbar^{-1}g(\omega)\sum V_{ij}^3/\sum V_{ij}^2\,, \qquad (3.8)$$

where we have used the fact that $V_{ij}>0$ for the S-N interaction. Similarly, the expression for the fourth moment[12] is modified by the replacements

$$(\sum_j V_{ij}^2)^2 \rightarrow [\hbar^{-1}g(\omega)V_{ij}^3]^2+\hbar^{-1}g(\omega)\sum_j V_{ij}^5$$
$$-\hbar^{-2}g^2(\omega)\sum_j V_{ij}^6\,, \qquad (3.9a)$$

$$\sum_j V_{ij}^4 \rightarrow \hbar^{-1}g(\omega)\sum_j V_{ij}^5\,, \qquad (3.9b)$$

and

$$\sum_{i\neq j\neq k\neq i} V_{ij}^2 V_{ik} V_{jk} \rightarrow \hbar^{-2}g^2(\omega) \sum_{i\neq j\neq k\neq i} V_{ij}^2 V_{ik}^2 V_{jk}^2\,, \qquad (3.9c)$$

so that using (2.16b) we find

$$(M_4)_{\text{in}}=\left[\frac{I(I+1)}{3}\right]^2 \Big\{5[\hbar^{-1}g(\omega)\sum_j V_{ij}^3]^2-\frac{2}{N}\hbar^{-2}g^2(\omega)$$
$$\times \sum_{i\neq j\neq k\neq i} V_{ij}^2 V_{ij}^2 V_{jk}^2 - 5\hbar^{-2}g^2(\omega)\sum V_{ij}^6$$
$$+\hbar^{-1}g(\omega)\left[8-\frac{3}{2I(I+1)}\right]\sum_j V_{ij}^5\Big\}\,. \qquad (3.10)$$

Using (3.8) and (3.10), we find the ratio of the fourth to the square of the second moment to be

$$\frac{(M_4)_{\text{in}}}{(M_2)_{\text{in}}^2}=\Gamma+\hbar g^{-1}(\omega)\left[8-\frac{3}{2I(I+1)}\right]\frac{\sum V_{ij}^5}{(\sum V_{ij}^3)^2}\,, \qquad (3.11)$$

where Γ is a number whose precise value depends upon d, but for all values of d is bounded by $-1<\Gamma<5$

(see Appendix B). Since we expect the model calculation to be meaningful only in the limit of large inhomogeneous broadening [i.e., $\hbar^{-1}g(\omega)M_2^{1/2}<1$], we may neglect Γ with respect to the remaining term in (3.11). In this limit we find, using (3.5), that

$$\left(\frac{1}{T_2}\right)_{\text{in}}^{\text{S-N}}=\tfrac{1}{6}\pi\sqrt{3}g(\omega)\left(\frac{A^2}{2Jz}\right)^2\left\{\frac{(\sum f_{ij}^3)^{3/2}}{(\sum f_{ij}^5)^{1/2}}\right\}$$
$$\times[\tfrac{1}{3}I(I+1)]^{1/2}\left[8-\frac{3}{2I(I+1)}\right]^{-1/2} \qquad (3.12)$$

with $f_{ij}\equiv f(\mathbf{r}_i-\mathbf{r}_j)$ being the distance dependence of the interaction defined by Eq. (2.6). All of the dependence of $1/T_2$ on the range of the interaction is now contained in the { } term. Equation (3.12) predicts a variation of $(1/T_2)_{\text{in}}^{\text{S-N}}$ with ω because of the factor $g(\omega)$; $(1/T_2)_{\text{in}}^{\text{S-N}}$ will diminish as ω moves away from ω_0 in either direction. Using the definition of M_2 for the perfect crystal we may express (3.12) in dimensionless form as

$$R^{\text{S-N}}(\Delta)\equiv\frac{(1/T_2)_{\text{in}}^{\text{S-N}}}{(\frac{1}{2}\pi)P(I)g(\omega)M_2}=\frac{(\sum f_{ij}^3)^{3/2}}{(\sum f_{ij}^5)^{1/2}(\sum f_{ij}^2)} \qquad (3.13)$$

with $P(I)=[8I(I+1)-1.5]^{-1/2}$. We point out that Eq. (3.13) is independent of the normalization of f_{ij} and that in particular in this expression we may replace f_{ij} by V_{ij}. For large values of I, we have $P(I)\rightarrow 8^{-1/2}I^{-1}$. In Fig. 3 we show a plot of $R^{\text{S-N}}(d)$ versus $1/\kappa$. That $R^{\text{S-N}}(d)$ should decrease as the range increases may be explained as follows: If we normalize the value of $(1/T_2)_{\text{in}}^{\text{S-N}}$ to a specific value of M_2 we are in fact requiring that the product $A^2/2Jz\sum_j f_{ij}^2$ remain constant. Now as $1/\kappa$ increases, $\sum_j f_{ij}^2$ increases, and hence $A^2/2Jz$ must decrease. But if the coupling constant decreases it becomes more and more difficult for two nuclei that are a given distance apart to satisfy the condition that their interaction energy is greater than or equal to the inhomogeneity. Thus, since an increasingly larger contribution to M_2 comes from more distant nuclei the larger is $1/\kappa$, and they in turn are increasingly less likely to satisfy the basic inequality $|\hbar\omega_{ij}|\leq V_{ij}$, we expect that, for a fixed M_2, the ratio $(1/T_2)_{\text{in}}^{\text{S-N}}/g(\omega)M_2$ will decrease with increasing $1/\kappa$.

2. *Dipolar Interaction*

We may use the same approach to derive expressions for M_2, M_4, and $1/T_2$ when dipolar interactions predominate and large microscopic inhomogeneities are present. For simplicity we treat the case of a simple cubic lattice of nuclear spins although the extension to other lattices is obvious. The basic dipolar interaction between two spins I_i and I_j is

$$d_{ij}=\tfrac{3}{2}\gamma^2\hbar(1-3\cos^2\theta_{ij})r_{ij}^{-3}, \qquad (3.14)$$

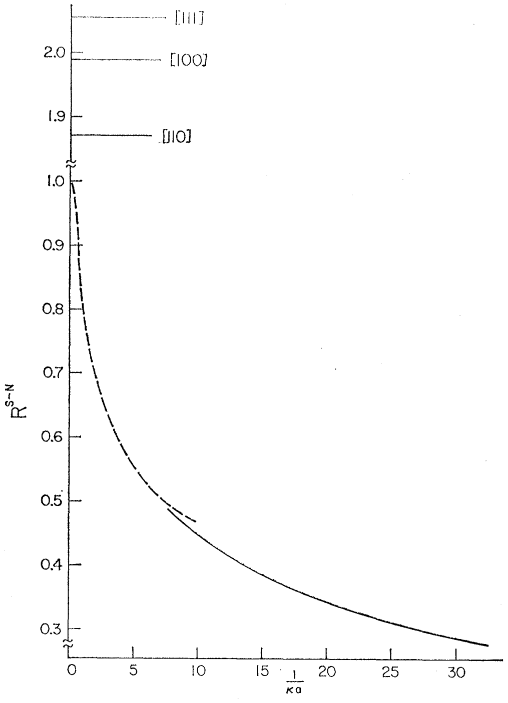

FIG. 3. The quantity $R^{\text{S-N}}$ as a function of $1/\kappa a$ for the bcc antiferromagnet. $R^{\text{S-N}}$ is defined by Eq. 3.13. The dashed line is the result obtained by direct summation over lattice sites extending to the lattice point (10,0,0). The solid line is the result obtained by replacing sums by integrals which is, again, the long wavelength approximation. For comparison, the quantities R^{dip} for the simple cubic lattice, as given in Table I, are also indicated on the figure. Note the break in the vertical scale between the dipolar and S-N functions.

where θ is the angle between the direction of the polarizing field and the radius vector $\mathbf{r}_{ij}$. The transcription to the inhomogeneous model is then

$$(M_2)_{\text{in}}=M_2\hbar^{-1}g(\omega)\frac{\sum d_{ij}^2|d_{ij}|}{\sum d_{ij}^2}, \qquad (3.15)$$

$$(M_4)_{\text{in}}=M_4'\hbar^{-1}g(\omega)\frac{\sum d_{ij}^4|d_{ij}|}{\sum d_{ij}^4}, \qquad (3.16)$$

where M_4' contains only that part of M_4 which is proportional to $\sum_j d_{ij}^4$. As in the inhomogeneous S-N calculation the reason for the truncation is that if $(M_4)_{\text{in}}/(M_2)_{\text{in}}^2$ is to be large compared to unity then the terms in M_4 that are linear in $g(\omega)$ must be large compared to the quadratic ones. It is to be noted that (3.15) and (3.16) are expressed as the sums of positive definite quantities since our inhomogeneous model requires only that the magnitude of the interaction of any given pair be larger than their corresponding frequency separation.

The quantities M_2 and M_4' are defined as

$$M_2=\frac{I(I+1)}{3}\sum_j d_{ij}^2 \qquad (3.17)$$

and

$$M_4'=\left[\frac{I(I+1)}{3}\right]^2\left\{\frac{7}{5}-\frac{3}{10I(I+1)}\right\}\sum_j d_{ij}^4. \quad (3.18)$$

The angular dependence of the interaction (3.14) necessarily results in the various lattice sums themselves being functions of the angle between the direction of the polarizing field and the crystal axes. Extremal values for $(M_2)_{\mathrm{in}}$ and $(M_4')_{\mathrm{in}}$ are obtained from calculations with the polarizing field oriented in the [100], [110], and [111] directions. Values for lattice sums appearing in $(M_2)_{\mathrm{in}}$, $(M_4')_{\mathrm{in}}$ and their ratio in $(M_4')_{\mathrm{in}}/(M_2)_{\mathrm{in}}^2$ in these three directions are given in Table I. Also given are the corresponding values of the quantity

$$R^{\mathrm{dip}}\equiv\left(\frac{8}{1.4}\right)^{1/2}\frac{(1/T_2)_{\mathrm{in}}{}^{\mathrm{dip}}}{(\frac{1}{2}\pi)Q(I)g(\omega)M_2}=\left(\frac{8}{1.4}\right)^{1/2}\frac{\sum(d_{ij}{}^2|d_{ij}|)^{3/2}}{\sum(d_{ij}{}^4|d_{ij}|)\sum d_{ij}{}^2}, \quad (3.19)$$

where $Q(I)=[1.4I(I+1)-0.3]^{-1/2}$. The factor $(1.4/8)^{1/2}$ has been introduced so as to normalize the spin-dependent factor $Q(I)$ to the corresponding factor $P(I)$ in Eq. (3.13) for $R^{\mathrm{S\text{-}N}}$ in the limit of large I. R^{dip} is seen to be relatively insensitive to field orientation and is therefore amenable to more direct comparison with the $R^{\mathrm{S\text{-}N}}$ of Eq. (3.14), as is shown in Fig. 3.

One interesting comparison may be made with Portis's spectral diffusion theory, applicable only to $I=\frac{1}{2}$. From completely different considerations he deduced that $(1/T_2)_{\mathrm{in}}{}^{\mathrm{dip}}/g(\omega)M_2\simeq1$, which is in essential agreement with the results of our model as shown in Table I. Since the Portis model is difficult to generalize to arbitrary spin values, we surmise that an approximate I dependence for his model might be obtained by analogy with our results,

i.e., $$\left[\left(\frac{1}{T_2}\right)_{\mathrm{in}}^{\mathrm{dip}}\Big/g(\omega)M_2\right](I)\approx\frac{Q(I)}{Q(\frac{1}{2})}.$$

TABLE I. Values of the sums appearing in the inhomogeneous model dipolar moments for the [100], [110], and [111] directions in a simple cubic lattice [see Eqs. (3.14), (3.15), and (3.16)]. The quantity d_{ij} is measured in dimensionless units of $\frac{3}{2}(\gamma^2\hbar/a^3)$, with γ the nuclear gyromagnetic ratio and a the lattice spacing. The quantity R^{dip} is defined by Eq. (3.19). Despite the pronounced anisotropy in $\sum|d_{ij}|^3$ and $\sum|d_{ij}|^5$ the quantity R^{dip} is almost isotropic. This situation is completely analogous to that found for $\sum d_{ij}{}^2$, $\sum d_{ij}{}^4$ and the ratio $M_4/M_2{}^2$ for the dipolar interaction in the perfect crystal; see pp. 112 and 113 of Ref. 7.

	$\sum\lvert d_{ij}\rvert^3$	$\sum\lvert d_{ij}\rvert^5$	R^{dip}
[100]	20.3	68.0	1.99
[110]	3.39	2.49	1.87
[111]	0.681	0.084	2.06

3. *Restrictions on Applicability of Inhomogeneous Model—Comparison with Experiment*

Before making any attempt to compare experiment with theory we must consider the limitations on the applicability of the model. The fundamental postulate of microscopic inhomogeneity presumes there to be no correlation between the difference in the resonance frequencies of a given pair of spins and their relative position. It is not difficult to visualize a situation where this assumption is violated although the entities (imperfections, etc.) which cause the inhomogeneous broadening are distributed at random. For example, suppose there were present, in an otherwise perfectly ordered magnetic lattice, a random but dilute distribution of vacancies. At any distance r from a given vacancy a "hole" dipolar field would be present which would, in a given direction, vary as the strength of the missing moment and diminish as r^{-3}. Since the nuclei that are closer to the vacancy will experience a larger displacement in their resonance frequencies while those that are more distant will be proportionately less affected it is clear that relative to the vacancy center there is a strong correlation between the separation in space and separation in resonance frequency for any given pair of nuclei.

From the above it might appear that it would be difficult to realize a situation in which the inhomogeneous broadening was microscopic if it was produced by a random array of imperfections. However suppose that, rather than the dilute concentration of causal imperfections, we had a relatively large concentration (i.e., >10%). Then nearly every nucleus would be affected by many imperfections, and the resonant frequency of any given nucleus would be the combined result of multiple changes in the local field. This would be particularly true for those nuclei whose resonance frequency remained the same as it was in the pure crystal. In this instance the difference in resonance frequencies for any pair of nuclei would tend to be uncorrelated with respect to their relative positions, since there would be numerous distinct spatial configurations of imperfections which would cause a given local field at a specific point.

Fortunately, the shape of the inhomogeneously broadened line allows one to distinguish between these two extreme cases. It is readily shown[16] that in the "dilute" imperfection limit the resonance profile, in the observable region, will assume a Lorentzian shape while in the high-concentration limit a Gaussian shape will be obtained. Hence, only in the latter case would one expect the inhomogeneous models that we have calculated to be strictly applicable. Any deviations from microscopic inhomogeneity will always result in the observed $(1/T_2)_{\mathrm{obs}}$ being bracketed by the relation $(1/T_2)_{\mathrm{in}}<(1/T_2)_{\mathrm{obs}}<(1/T_2)_{\mathrm{hom}}$.

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[16] M. H. Cohen and R. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

Keeping these limitations in mind we consider the relevance of the inhomogeneous model to three particular resonances: first, that of Mn^{55} in MnF_2 where the S-N interaction is large compared with the dipolar interaction; second, that of F^{19} in the same crystal where the Mn^{55}-Mn^{55} S-N interaction modifies the F^{19} dipolar interaction and lastly the F^{19} resonance in FeF_2, where the dipolar interaction alone is of any importance.

Whichever of the spin-spin interactions is most important, the criterion for the applicability of the inhomogeneous model is that

$$M_2^{1/2}[\hbar g(\omega)]^{-1} \ll 1\,. \tag{3.20a}$$

Furthermore, if the decay of the echo envelope is to be exponential the truncated Lorentzian line shape should apply and therefore

$$(M_4)_{\text{in}}/(M_2)_{\text{in}}^2 \gg 1\,. \tag{3.20b}$$

At the center of the resonance $g^{-1}(\omega_0)\approx\Delta$, the full linewidth of the inhomogeneously broadened resonance.

Mn^{55} in MnF_2. Clearly with $M_2^{\text{S-N}}$ for the Mn^{55} resonance equal to $(\sim 350\text{ Oe})^2$ it would require an inhomogeneous linewidth considerably in excess of 10^2 Oe for an appreciable reduction in $(M_2^{\text{S-N}})_{\text{in}}$ to occur and for the inequality (3.20b) to be satisfied. The magnetic hyperfine interaction of the Mn^{2+} ion arises primarily from intra-atomic core polarization and, to a large degree, is insensitive to strains and imperfections in the crystal. We estimate the inhomogeneous broadening of the Mn^{55} NMR in MnF_2, if any, to be much less than 10^2 Oe. Experiment[17] confirms this surmise in that the resonance appears to be homogeneously broadened and the observed and calculated linewidths agree.

F^{19} in MnF_2. This resonance has been studied[4,18] in a number of samples including some which were further inhomogeneized by doping. In each case it has been noted, from transient experiments, that for the inhomogeneously broadened resonance

$$\Delta > (M_2^{\text{S-N}}+M_2^{\text{dip}})^{1/2} > \left(\frac{1}{T_2}\right)_{\text{hom}}\,. \tag{3.21}$$

(Although $M_2^{\text{dip}} > M_2^{\text{S-N}}$ a complete treatment of the F^{19} linewidth in MnF_2 necessitates keeping both S-N and dipolar-interaction terms in calculating the total M_2 because of possible destructive interference effects. These are discussed in Appendix D.) Before considering the inhomogeneously broadened case it is to be noted, and explained, that the perfect crystal line shape in this particular case should be more Lorentzian than Gaussian. The details again are discussed in Appendix D. They amount to the fact that the combination of a relatively weak Mn^{55}-F^{19} dipolar interaction and a strong Mn^{55}-Mn^{55} S-N interaction result in a large increase in the F^{19} M_4 and hence narrow the line appreciably. A numerical calculation[19] gives for the modified fourth moment

$$M_4^*(\text{F}) \simeq M_4(\text{F}) + \tfrac{1}{3}M_2^{\text{S-N}}(\text{Mn})M_2^{\text{dip}}(\text{F-Mn})\,, \tag{3.22}$$

where $M_4(\text{F})$ is obtained from dipolar interactions alone. We find $M_4^* = 2.2\times10^{-87}$ erg^4, using $M_2^{\text{S-N}}(\text{Mn}) = 2.3\times10^{-42}$ erg^2 and $M_2^{\text{dip}}(\text{Mn-F}) = 3\times10^{-45}$ erg^2. The calculated [using the cutoff Lorentzian expression Eq. (3.5)] and observed values of T_2^{19} for the "perfect" crystal are

$$(T_2^{19})_{\text{calc}} = 100\ \mu\text{sec and } (T_2^{19})_{\text{obs}} = 30\ \mu\text{sec}, \tag{3.23}$$

respectively. The magnitude and direction of the discrepancy is similar to that which has been found for exchange narrowed nuclear magnetic resonances in paramagnets.[20] The situation with respect to the inhomogeneously broadened crystals is somewhat more complicated and the details will be given elsewhere.[18] The qualitative features are as follows: Some nominally pure crystals show an inhomogeneously broadened *Gaussian*-shaped line of width $\Delta \simeq 14$ Oe and hence satisfy the requirements set forth above for the applicability of the inhomogeneous model. (The inhomogeneities probably result from a high concentration of strain fields.) For small inhomogeneous broadening the "like" F^{19} spins are detuned and $M_2^{\text{dip}}(\text{F-F})$ is reduced. However, $M_2^{\text{dip}}(\text{F-Mn})$ is independent of inhomogeneities, to a first approximation, because of the I_z^{55}-I_z^{19} longitudinal character to the dipolar interaction between unlike spins. Therefore, $M_4^*(\text{F})$ remains essentially unchanged while $(M_2)_{\text{in}}$ decreases and thus $(1/T_2)_{\text{in}}$ tends to decrease. However, when the crystals are deliberately inhomogeneized by the addition of magnetic (or nonmagnetic) impurities, there results a proportionately smaller reduction in $1/T_2$ than would be expected from the size of Δ. But here the inhomogeneous line profile is more Lorentzian indicating that the inhomogeneity is not of a microscopic nature.

F^{19} in FeF_2. For the F^{19} NMR in FeF_2 the S-N F^{19}-F^{19} contribution is entirely negligible in comparison with the dipolar one. This is a consequence of the huge gap in the spin-wave spectrum at $k=0$ due to the large single-ion anisotropy. For this latter reason and because the Fe^{57} nuclei have small moments and are in low abundance, there is no appreciable contribution to $M_4^*(\text{F})$ as there was in the MnF_2 case. Hence were

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[17] H. Yasuoka, Tin Ngwe, V. Jaccarino, and H. J. Guggenheim, Phys. Rev. **177**, 667 (1969). To be more precise the experiment shows that the Mn^{55} resonance is split into five quadrupolar lines whose relative intensities and linewidths agree with the S-N theory, appropriately corrected and extended. Moreover a careful transient experiment was performed and neither spin echoes nor a free induction decay were found thereby allowing an upper limit to be placed on T_2, which is again in agreement with the theory.

[18] M. Butler, N. Kaplan, V. Jaccarino, and H. J. Guggenheim (unpublished).

[19] We are indebted to M. Butler and J. Gulley for this result.

[20] J. Gulley, B. Silbernagel, and V. Jaccarino, Proceedings of the 14th Annual Magnetism Conference, New York, 1968 (unpublished); J. Appl. Phys. **40**, 1318 (1969).

there no inhomogeneity present, an approximately Gaussian-shaped line would result with a value of $M_2^{\text{dip}}(\text{F-F}) = 3.2 \times 10^{-45}$ erg^2. This corresponds to a derivative extrema separation $\delta H = 4.3$ Oe. In the crystal that has been studied[18] the observed line profile is Gaussian but it is inhomogeneously broadened to the extent that $\delta H = 11$ Oe. Using the inhomogeneous model [Eq. (3.19)] we find $(T_2)_{\text{in}}^{\text{dip}} \simeq 90$ μsec whereas $(T_2)_{\text{obs}} \simeq 30$ μsec. The discrepancy in this case may reflect the limitations of the model when Eq. (3.20a) is not strictly satisfied or that the inhomogeneity is not truly microscopic.

4. *Other Approaches to the Problem of Inhomogeneous Broadened Lines*

The general problem of inhomogeneously broadened resonance lines has been approached from an entirely different point of view by Klauder and Anderson[21] (K-A). Since the underlying assumptions of the K-A model and the experiments to which it is applicable differ to some extent from the ones considered above, we feel some comparisons between the two theories is appropriate. Klauder-Anderson considered the problem of spectral diffusion in spin-echo decays in an inhomogeneously broadened line. Their model presumes that there are two classes of spins: a small group "*A*," the ones under observation, whose resonance frequencies are contained with an interval $\delta\nu \simeq \gamma H_1$ of the mean frequency of the echo-producing r-f oscillator and a group "*B*," which are all the remaining spins in the sample. The "*A*" spins are so few in number that interactions among themselves may be neglected, and hence only "*A*"−"*B*" and "*B*"−"*B*" interactions need be considered. Furthermore the "*A*" and "*B*" spins are thought to be so unlike that only the $I_{zi}^A I_{zj}^B$ part of the dipolar interaction is secular and the remaining part is treated as a small perturbation. Hence, most of the homogeneous broadening is "diagonal in nature" in the K-A model. The K-A theory finds ready application in electron paramagnetic resonance experiments[22] in which the total number of spins ("*A*"+"*B*") in the sample is much less than the number of lattice sites. In this limit[16] the line is inhomogeneously broadened and the profile $g(\omega)$ is Lorentzian. Spectral spin diffusion of the resonance "*A*" spins is measured by two and three pulse spin-echo experiments.[22]

Our microscopic inhomogeneous broadening model really applies to a "dense" crystal where like and unlike spins are distinguished by the criteria $\rho_{ij} \geq 1$ and $\rho_{ij} < 1$, respectively. As mentioned earlier, for the model to be applicable we would require that the inhomogeneous line profile be Gaussian. We pretend to no knowledge about spectral diffusion, since we make comparison only with those two-pulse spin-echo experiments in which the decay of the entire transverse magnetization is studied; a condition obtained by making $\gamma H_1 > [g(\omega_0)]^{-1}$.

There are certain inherent limitations in the use of both models which are apparent. The K-A approach, as formulated, would not apply to the S-N case, because there is no $I_i^z I_j^z$ part to this interaction. The criterion imposed by our model presupposes that one can treat each spin as having a well-defined resonance frequency at any instant of time. There is, in fact, only an elementary excitation at that frequency with an uncertainty in frequency of the order of $1/T_2$, as K-A have pointed out. This frequency width for the two interacting spins could, in principle, be folded into our two-spin "yes-no" criterion as an approximate way of including the many-body aspects of the real problem. Clearly this correction becomes less important the larger is the relative size of the inhomogeneous to homogeneous broadening.

Our mutual spin-flip criterion would appear to neglect the contribution that is made by the $I_i^z I_j^z$ part to $1/T_2$ in treating the dipolar interaction. Actually we used the entire dipolar Hamiltonian in evaluating all of the moments. We believe this to be a valid procedure in that limit where there is only one spin species and where all of the spins are contained within the resonance profile. Then in a two-pulse spin-echo experiment with $\gamma H_1 > [g(\omega_0)]^{-1}$, the homogeneous broadening resulting from the random frequency modulation of the $I_i^z I_j^z$ terms by further $I_j^+ I_k^-$ interactions contributes in the same proportion as it does in the perfect (homogeneous) crystal.

ACKNOWLEDGMENTS

We sould like to thank Dr. M. Bulter and Dr. N. Kaplan for a number of discussions concerning the experimental aspects of the problem and the limitations imposed by the postulate of micorscopic inhomogeneity upon the applicability of models considered. We are indebted to Dr. T. Nakamura for a communication on his original work and for some of the numerical results included in the table of Appendix A. Dr. P. Richards of the University of Kansas has independently obtained the result contained in Eq. (2.18), and we wish to express our appreciation for a preprint of his work.

APPENDIX A: EVALUATION OF SUMS IN EQS. (2.19) AND (2.21)

As was indicated in Ref. 2, momentum integrals such as those found in Eqs. (2.19) and (2.21) can be evaluated numerically after reduction to one-dimensional form with arguments that contain complete elliptic

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[21] J. R. Klauder and P. W. Anderson, Phys. Rev. **125**, 912 (1962).

[22] W. B. Mims, K. Nassau, and J. D. McGee, Phys. Rev. **123**, 2059 (1961).

integrals. For example,

$$\frac{1}{(2\pi)^3}\iiint_0^{2\pi} dq_1dq_2dq_3\frac{f(\cos q_3)}{(1+d^2)^2-\gamma_q^{\,2}}=\frac{2}{\pi^2(1+d^2)^2}\times\int_0^{\pi} dq_3\, F\left(\frac{\pi}{2},\frac{\cos\frac{1}{2}q_3}{1+d^2}\right)f(\cos q_3)\,, \tag{A1}$$

where $\gamma_q=\cos\frac{1}{2}q_1\cos\frac{1}{2}q_2\cos\frac{1}{2}q_3$, as usual, $F(\pi/2,k)$ is a complete elliptic integral of the first kind with modulus k, and $f(x)$ is an arbitrary function of x. We also have need of the result, again obtained by straightforward integration over two of the three Cartesian coordinates,

$$\frac{1}{(2\pi)^3}\iiint_0^{2\pi} dq_1dq_2dq_3\frac{f(\cos q_3)}{[(1+d^2)^2-\gamma_q^{\,2}]^2}=\frac{1}{\pi^2(1+d^2)^2}\times\int_0^{\pi} dq_3\left\{(1+d^2)^{-2}F\left(\frac{\pi}{2},\frac{\cos\frac{1}{2}q_3}{1+d^2}\right)+[(1+d^2)^2-\cos^2\tfrac{1}{2}q_3]^{-1}E\left(\frac{\pi}{2},\frac{\cos\frac{1}{2}q_3}{1+d^2}\right)\right\}f(\cos q_3)\,, \tag{A2}$$

where $E(\frac{1}{2}\pi,k)$ is a complete elliptic integral of the second kind with modulus k. We define, in addition,

$$F_n=\frac{1}{\pi^2(1+d^2)^n}\int_0^{\pi} F\left(\frac{\pi}{2},\frac{\cos\frac{1}{2}q}{1+d^2}\right)\cos^n(\tfrac{1}{2}q)\,dq\,,$$

$$E_n=\frac{1}{\pi^2(1+d^2)^n}\int_0^{\pi} E\left(\frac{\pi}{2},\frac{\cos\frac{1}{2}q}{1+d^2}\right)\times\left[1-\frac{1}{(1+d^2)^2}\cos^2(\tfrac{1}{2}q)\right]^{-1}\cos^n(\tfrac{1}{2}q)dq\,, \tag{A3}$$

$$G=\frac{1}{\pi^2}\int_0^{\pi}\left\{\pi-3F\left(\frac{\pi}{2},\frac{\cos\frac{1}{2}q}{1+d^2}\right)+\left[1-\frac{\cos^2(\frac{1}{2}q)}{(1+d^2)^2}\right]\times E\left(\frac{\pi}{2},\frac{\cos\frac{1}{2}q}{1+d^2}\right)\right\}\sec^2\left(\frac{q}{2}\right)dq\,.$$

Then with the corrected signs in Eq. (2.21) we find, instead of Eqs. (28) and (29) of Ref. 2,

$$f=(F_0+E_0)\alpha^2\,, \tag{A4}$$

$$f'/\alpha=32-(96-8\alpha-\alpha^2)F_0+8(2+\alpha)F_2+16F_4+(32-8\alpha+\alpha^2)E_0-8(2-\alpha)E_2+16E_4-32G\,, \tag{A5}$$

where $\alpha=(1+d^2)^{-2}$. For small d we can take $\alpha=1$ in the coefficients (but not in the integrands of F_n, E_n, and G). In the limit $d^2\rightarrow 0$ all F_n remain finite, but $G\approx E_n\approx 1/\pi d\sqrt{2}$. In this limit

$$f\approx f'\approx 1/\pi d\sqrt{2}\,. \tag{A6}$$

Finally, we give in Table II the values of f and f' for the representative values of d used in Ref. 2 (where $1+\Delta^2=\alpha^{-1}$). The value $d=0.126$ is appropriate to MnF_2.

TABLE II. Values of the quantities appearing in the S-N second moments for the magnetic ions [f and $f(0)$] and the nonmagnetic ions [f' and $\tilde{f}(0)$] in rutile structure antiferromagnets.

Δ	d	f	$f(0)$	$f-f^2(0)$	f'	$\tilde{f}(0)$	$f'-\tilde{f}^2(0)$
0.1	0.0706	4.08	1.33	2.31	14.06	3.02	4.94
0.179	0.1261	2.54	1.25	0.98	11.64	2.79	3.87
0.224	0.1574	2.12	1.21	0.66	10.46	2.63	3.54

APPENDIX B: S-N FOURTH MOMENT CALCULATION

In Eq. (2.16b) we have given an expression for the fourth moment of a line homogeneously broadened by the S-N interaction:

$$M_4=\left[\frac{I(I+1)}{3}\right]^2\left[5(\sum_j V_{ij}^{\,2})^2-\frac{2}{N}\sum_{i\neq j\neq l\neq i} V_{ij}^{\,2}V_{il}V_{jl}+3\left(1-\frac{1}{2I(I+1)}\right)\sum_j V_{ij}^{\,4}\right]. \tag{B1}$$

The first of the three terms on the right-hand side is just $5M_2^{\,2}$. The third term, involving $V_{ij}^{\,4}$, drops off rapidly with $|\mathbf{r}_i-\mathbf{r}_j|$; numerical evaluation for values of $H_A/H_E<0.5$ verified that it is negligible with respect to the first term. The remaining term has been discussed in Ref. 13, but we wish to correct the conclusions of that paper. Neglecting the last term in Eq. (B1) we have

$$R=M_4/M_2^{\,2}=5-(2/N)\sum_{i\neq j\neq l\neq i} V_{ij}^{\,2}V_{il}V_{jl}/(\sum_j V_{ij}^{\,2})^2. \tag{B2}$$

Since the S-N interaction function V_{ij} is positive for all lattice sites i and j, the ratio (B2) is necessarily less than 5. Thus, the estimate of 6 obtained in Ref. 13 must clearly be in error.

We can readily obtain a *lower* limit on this moment ratio by using the form (2.16c) for the fourth moment. Then we have

$$5>R=3+N^{-1}\sum V_{ij}^{\,2}(V_{ij}-V_{jl})^2/(\Sigma\, V_{ij}^{\,2})^2>3; \tag{B3}$$

the ratio is thus bracketed between 3 and 5, and the predicted line shape is very nearly Gaussian. In the small-anisotropy (long-range) limit we can, as in Ref. 13, replace the sum in Eq. (B.2) by an integral, ignoring the restrictions on i, j and l. In the limit we can use the asymptotic form for $V(\mathbf{r}_i-\mathbf{r}_j)$

$$V(r)\propto f(r)=e^{-\kappa r}/\pi r$$

and we can conveniently choose as integration variables $r_1 \equiv r_{ij}$, $r_2 \equiv r_{il}$, and $r_{12} \equiv |\mathbf{r}_{ij} - \mathbf{r}_{il}|$. Then we find

$$\frac{1}{N}\sum f_{ij}^2 f_{il} f_{jl} \approx \frac{8}{\pi}\int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_{12} \frac{e^{-\kappa r_{12}} e^{-\kappa r_2} e^{-2\kappa r_1}}{r_1} = \frac{8}{3\pi\kappa^2}. \tag{B4}$$

In the same approximation $\sum f_{ij}^2 \approx 2/\pi\kappa$, so

$$R \approx 5 - \tfrac{4}{3} = 11/3, \quad (\kappa \to 0). \tag{B5}$$

In a similar fashion we can find bounds for the moment ratio in the presence of inhomogeneity. In the limit of strong inhomogeneities, as discussed in Sec. III, the last term in M_4 is reduced by one lower power of $g(\omega)$ than are the other two and eventually, therefore, it dominates $(M_4)_{\text{in}}$. It is the remaining terms we wish to bound

$$\Gamma \equiv 5 - \frac{2}{N}\frac{\sum V_{ij}^2 V_{il}^2 V_{jl}^2}{(\sum V_{ij}^3)^2}. \tag{B6}$$

Again it is clear that $\Gamma < 5$. We have, furthermore, the inequality

$$V_{ij}^2 V_{il}^2 V_{jl}^2 < V_{ij}^3 V_{il}^3 + V_{ij}^3 V_{jl}^3 + V_{il}^3 V_{jl}^3, \tag{B7}$$

so that

$$-1 < \Gamma < 5,$$

where we have dropped terms like $\sum V_{ij}^6$ relative to $(\sum V_{ij}^3)^2$ with the same justification we have given above for the neglect of the final term in (B1).

APPENDIX C: SPINS $\frac{1}{2}$ COUPLED BY EXCHANGE INTERACTION

We consider here two spins $\frac{1}{2}$ coupled by a transverse exchange interaction, for the purpose of investigating the influence on the efficiency of the mutual spin-flip process of a difference in the magnetic fields at the two sites. The appropriate Hamiltonian is

$$\mathcal{H} = -h_1 I_1^z - h_2 I_2^z + \tfrac{1}{2} J (I_1^+ I_2^- + I_1^- I_2^+), \tag{C1}$$

where h_i is the product of the g factor, the nuclear magneton, and the magnetic field at i. $\mathcal{H}$ is trivially diagonalized; the parallel-spin eigenstates of the Zeeman Hamiltonian are unaffected by the exchange interaction and the antiparallel-spin states are mixed to give (unnormalized) eigenstates

$$|\psi\rangle = |\uparrow\downarrow\rangle + [J/(h_1 - h_2 - 2\omega)]|\downarrow\uparrow\rangle, \tag{C2}$$

where the energies are

$$\omega = \pm\tfrac{1}{2}[J^2 + (h_1 - h_2)^2]^{1/2}. \tag{C3}$$

The mutual spin-flip frequency is then measured by the square of the ratio of the amplitudes of $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ in (C2),

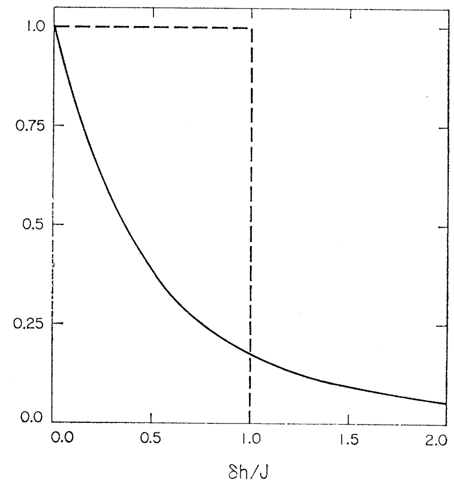

FIG. 4. Spin-flip rate of two exchange-coupled spins $\frac{1}{2}$ as defined by Eq. (C4), given here by the solid line. The dashed line represents the approximation employed in Sec. III for this efficiency in the many-spin system. The abscissa is the ratio of the difference in Zeeman energies at the two sites to the exchange-interaction strength J.

$$f(h_1 - h_2) \equiv J^2 / \{(h_1 - h_2) + [J^2 + (h_1 - h_2)^2]^{1/2}\}^2 \tag{C4}$$

which is plotted in Fig. 4.

The approximation we have made in Sec. III, as applied to this two-spin system, is to replace $f(h_1 - h_2)$ by the step function

$$\begin{aligned} f_0(h_1 - h_2) &= 1, \quad \text{when } |h_1 - h_2| < J \\ &= 0, \quad \text{when } |h_1 - h_2| > J. \end{aligned} \tag{C5}$$

This seems to indicate that the detuning effects of inhomogeneity may be even more severe than implied by our model. However, the relevance of the two-spin behavior to that of the actual many-spin problem is limited. Each spin is exchange coupled to many others and thereby acquires a smooth spectral distribution of spin-flip frequencies around, but not uniquely located at the local Zeeman frequency. The overlap of these spectral functions at two sites is then a measure of the part played by energy conservation requirements in the mutual spin-flip probability of these two spins. Thus, the exchange of each with all other spins, which is left out of the two-spin picture, should be considered for a more complete understanding of the validity of our model. However, we feel that the much simpler two-spin calculation is sufficient to indicate the suitability of our model as an approximate description of the systems we consider.

APPENDIX D: DIPOLAR INDUCED CORRECTIONS

In this appendix we show explicitly how the dipolar induced corrections to the F^{19} linewidth in MnF_2 (which we discussed in Sec. III and Ref. 4) arise. If we denote the F^{19} nuclear spins by **I** and the Mn^{55} spins by **J**, the relevant Hamiltonian has the form

$$\mathcal{H}=\sum_{i\neq j} A_{ij}\mathbf{I}_i\cdot\mathbf{I}_j+\sum_{i\neq j} B_{ij}I_i^zI_j^z+\sum_{i\neq j}C_{ij}I_i^zJ_j^z \\ -\sum_{i\neq j} U_{ij}I_i^+I_j^- -\sum_{i\neq j} V_{ij}J_i^+J_j^-, \quad \text{(D1)}$$

where the symbols are as follows: A_{ij} is the isotropic part of the F^{19}-F^{19} dipolar interaction; B_{ij} is the anisotropic part of the F^{19}-F^{19} dipolar interaction; C_{ij} is the anisotropic part of the F^{19}-Mn^{55} dipolar interaction; $U_{ij}=F^{19}$-F^{19} S-N interaction; and $V_{ij}=Mn^{55}$-Mn^{55} S-N interaction. The usual truncation of the nonsecular terms has already been made in Eq. (D1), and the Mn^{55}-Mn^{55} dipolar interaction has been neglected because it is of no significance in calculations of the F^{19} moments. It is important to notice that by far the largest interaction in (D1) is V_{ij}; this is, of course, due to the large Mn^{55} hyperfine interaction. The second moment of the F^{19} NMR line is then[12]

$$M_2=\tfrac{1}{3}I(I+1)\sum_j (B_{ij}+2U_{ij})^2+\tfrac{1}{3}J(J+1)\sum_k C_{ik}^2, \quad \text{(D2)}$$

where the j ranges over all F^{19} nuclei for the B_{ij} terms but only over a given sublattice for the U_{ij} terms; k ranges over all the Mn^{55} spins.

Here

$$B_{ij}=-3g^2\beta^2\gamma_{ij}^2r_{ij}^{-3}, \quad \text{(D3)}$$

where γ_{ij} is the direction cosine of $\mathbf{r}_{ij}$ relative to the z axis; note that B_{ij} is negative definite while U_{ij} is positive definite—thus, there is somewhat of a tendency for the longitudinal anisotropic part of the dipolar interaction to combine with the transverse S-N interaction and become isotropic and hence *not* contribute to M_2. If $|B_{ij}|$ and $|U_{ij}|$ were comparable, this destructive interference would be significant. This was thought to be the case in MnF_2, where a 20% reduction in M_2 was estimated[4] for the homogeneous crystal, when it was assumed $|U_{ij}|>|B_{ij}|$. Since we now know that the F^{19}-F^{19} S-N interaction is much smaller than the corresponding dipolar interaction the importance of the above considerations is considerably less than had been first anticipated.

However, what is an important contribution to the line narrowing in MnF_2 arises from the interplay of the F^{19}-Mn^{55} dipolar interaction and the Mn^{55}-Mn^{55} indirect coupling. This gives a contribution to the fourth moment of the fluorine line in addition to that of the S-N interaction considered in Sec. 2. Again from Van Vleck,[11] we find

$$M_4^*(F)\cong M_4^{\text{S-N}}(F)+8[\tfrac{1}{3}J(J+1)]^2 \\ \times\sum_{l>k} V_{kl}^2(C_{jk}-C_{jl})^2. \quad \text{(D4)}$$

The second term is important because of the large value of V_{kl}. When V_{kl} is relatively long-ranged (compared to the dipolar interaction), (D4) may be very crudely estimated as

$$M_4^*(\mathrm{F})\approx M_4^{\text{S-N}}(\mathrm{F})+M_4^{\text{S-N}}(\mathrm{Mn})M_2^{\text{dip}}(\text{F-Mn}). \quad \text{(D5)}$$

A more precise calculation[19] using the parameters appropriate to MnF_2 yields the result given in Eq. (3.22).