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[11] It is important to note that there is a second susceptibility, $(\partial M/\partial H)_{T,S}$, which is in general different from the above susceptibility, $(\partial M/\partial H)_{T,\xi}$. In fact, as we will see, $(\partial M/\partial H)_{T,\xi}$ diverges at any point on the coexistence curve for all values of the dimensionality greater than 2, whereas $(\partial M/\partial H)_{T,S}$ also diverges on the coexistence curve for three- and four-dimensional lattices, but remains finite for dimensionality greater than 4. The divergence of $(\partial M/\partial H)_{T,\xi}$ on the coexistence curve corresponds to the vanishing of the inverse correlation length κ_+ defined in Eq. (2.18). There is, however, a natural inverse length κ_- which arises in the dynamical analysis and which is nonzero on the coexistence curve for all values of dimensionality.

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Spin Correlations in Impure Linear Heisenberg Chains*

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We present calculations of the high-temperature time-dependent two-spin correlation functions in impure one-dimensional Heisenberg chains. The dynamics is assumed to be dominated by diffusion, which is obtained as the continuous time limit of a random walk of spin along the chain. The correlations are calculated in the presence of finite concentrations of both nonmagnetic and strongly spin-lattice-coupled impurities. Application is made to the determination of position-dependent (relative to an impurity) NMR linewidths in the presence of hyperfine or electron-nuclear dipole interactions. In the case of spin-lattice-coupled impurities and for short enough chains, the NMR line shape is found to be Lorentzian with a width significantly less than that found in pure chains. The width is found to depend approximately linearly on distance from the nearest impurity. In the case of nonmagnetic impurities, the line shape is found to be Lorentzian in the wings but Gaussian near the center. No narrowing of the resonance is found above that for the pure chain, and the position dependence is such as to increase the width near an impurity.

I. INTRODUCTION

Early interest in magnetic linear chains was primarily associated with the vastly greater simplicity of analysis possible as compared with the corresponding three-dimensional systems.[1] Exact calculations were of particular importance in analyzing general features of magnetic behavior as well as in providing tests of approximate methods used both in three and in lower dimensions. However, with the discovery of a growing number of real materials whose magnetic behavior is governed by one-dimensional exchange Hamiltonians,[2] attention has focused on describing both the thermodynamic and dynamic properties of these physical systems. In many of them the exchange is very nearly isotropic. The thermodynamics of such Heisenberg linear chains has been studied[3] (for spin $\frac{1}{2}$) for chains of finite length, by numerical techniques which exactly diagonalize the Hamiltonian. Convergence with increasing length suggests reasonable extrapolations for infinite chains. Similar calculations have been carried out[4] for the dynamical properties.

It was recognized that crystal imperfections could lead to the existence of finite chains in the physical systems studied experimentally, but calculational time limitations made studies of chains longer than 11 spins prohibitive, whereas indications[5,6] are that lengths of the order of 30–50 or more spins are playing an important role in systems of current experimental interest. More generally, impurities with magnetic properties very different from those of the host will strongly affect spin dynamics—particularly local behavior near the impurities. With this in mind we consider here an approximate calculation of spin dynamics in Heisenberg linear chains with impurities at arbitrary separations. We concentrate on two interesting limiting cases—the nonmagnetic impurity and the magnetic impurity strongly (spin-orbit) coupled to the lattice, which modifies spin correlations by rapidly dissipating spin information which reaches it. In both cases the system is effectively broken up into noncommunicating finite chains.

As a model we have chosen a description of exchange dynamics by a hopping process, or random walk, of spin excitations along the chain. This picture has been very successful in describing the behavior of (Frenkel) triplet excitons in alternating Heisenberg linear chains in crystals of aromatic organic molecules.[2,7] More recently, a similar description proved essential to an understanding of the spin correlations in the linear chain crystal $(CH_3)_4NMnCl_3$ (TMMC) as observed in the high-temperature EPR, where experiment and theory are now in detailed agreement.[2,8] In the infinite chain, at times t much greater than the exchange time, the hopping picture predicts $t^{-1/2}$ behavior for correlation functions, characteristic of any diffusion process. The consequent $\omega^{-1/2}$ low-frequency divergence of the frequency Fourier transform of the correlation functions is suggested[4] by the numerical analysis for finite chains and, not surprisingly, it is found[9] in analytic approximations based on reasonable assumed forms of the generalized diffusivity. This $t^{-1/2}$ behavior is the dominant feature of the high-temperature spin dynamics, but at lower temperatures development of short-range order is exhibited in the formation of relatively long-lived "sloppy spin waves," seen both in neutron-scattering experiments[10] and in finite-chain calculations.[11] Our model is clearly inappropriate when these correlations become important; it is applicable only to systems at temperatures well above the effective exchange energy. In the organic crystals, where this energy is itself strongly temperature dependent, the model may well be appropriate over the whole experimental temperature range.

We are interested here especially in local spin correlations and their dependence on the distance of the spins involved from impurities. Magnetic-resonance experiments probe such correlations, although somewhat indirectly. The relaxation function

$$\varphi(t) \equiv \langle M_x(t) M_x(0)\rangle / \langle M_x^2(0)\rangle , \qquad (1.1)$$

which describes the decay of a spatially uniform nonequilibrium magnetization M_x, is by the fluctuation-dissipation theorem essentially the time Fourier transform of the resonance line shape[12] (for rf field in the x direction). In turn, the equation of motion of $\varphi(t)$ in the interaction representation, where the perturbation H' is the line-broadening mechanism (e.g., dipolar or hyperfine interactions), relates it to an equilibrium correlation function $\psi(t) \propto \langle [M_x(t), H'(t)][M_x, H']\rangle$:

$$\varphi(t) \approx \exp\left[-\langle \omega^2\rangle \int_0^t d\tau (t-\tau)\psi(\tau)\right] . \qquad (1.2)$$

Here $\langle \omega^2\rangle = \frac{1}{2}\ddot{\varphi}(0)$ is by definition the second moment of the resonance line if $\psi(\tau)$ is normalized to $\psi(0)=1$. The time dependence of operators in $\psi(\tau)$ is generated by the unperturbed Hamiltonian (without H'). This expression for $\varphi(t)$ is exact if H' represents a Gaussian random process, which seems to be an adequate approximation for exchange-modulated interactions even in one-dimensional systems.[8] The observed line shape gives $\varphi(t)$, at least at long times, and thereby information on $\psi(\tau)$.

The structure of $\psi(\tau)$ is simplest for NMR if H' corresponds to a hyperfine or electron-nuclear dipole interaction. Then we need calculate only $\langle S_i^z(t) S_j^z(0)\rangle$, where $|r_i - r_j|$ extends only over the range of the coupling. Variation in hyperfine or dipolar energies with distance from an impurity can separate NMR lines appropriate to spins at different positions relative to impurities, so that the dynamics of these various spins can be studied experimentally. These two-spin correlation functions are precisely what the hopping picture is set up to calculate, and in Secs. II–IV we study them as functions of impurity parameters and of spin positions r_i and r_j, relative to each other and to the impurities. The applicability of these functions to the common case in EPR where H' arises from electronic dipolar interactions is less clear, but it appears[8] that factorization of the relevant four-spin into products of two-spin correlation functions may be a sensible approximation there.

In Sec. II we illustrate our model by calculating $\psi(\tau)$ for the two cases of single nonmagnetic and strongly spin-lattice-coupled impurities. In Sec. III we calculate $\psi(\tau)$ for finite impurity concentrations and apply these results in Sec. IV to nuclear magnetic resonance.

II. MODEL

We obtain the dominant physical process of diffusion as the continuous time limit of a random walk. Thus the essential parameters in the theory are the hopping probabilities per unit time (proportional to the exchange coupling, J and J' for host and impurity, respectively) and, if applicable, the rate of spin loss to the lattice. Given these, the model we adopt is exactly soluble.

A. Single Impurity with Different Exchange

As illustrative of the model we consider just the case of a single impurity having exchange coupling $J' \neq J$ situated at the origin of an infinite one-dimensional chain. We characterize the spin of a particular site as having a set of hopping probabilities to its nearest neighbors. During the discrete time interval Δt, the spin of site i has the option either to hop to sites $i \pm 1$ with the probabilities $P_{i,\,i\pm1}$ or to remain on site i with the probability $P_{ii} = 1 - P_{i,\,i-1} - P_{i,\,i+1}$. In the presence of an impurity these hopping probabilities are no longer uniform throughout the chain:

$$\begin{aligned} &P_{ij} = 0 \quad \text{if } j \neq i, \quad i \pm 1 \;, \\ &P_{i,\,i\pm1} = P + \Delta P(\delta_{i,\mp1} + \delta_{i,0}) \;, \qquad\qquad (2.1) \\ &P_{i,\,i} = 1 - 2P - \Delta P(2\delta_{i,0} + \delta_{i,1} + \delta_{i,-1}) \;. \end{aligned}$$

The limit of a nonmagnetic impurity is obtained when $\Delta P = -P$.

Let the random walk begin on the site j and terminate at time $n\Delta t$ on the site i. The walk is then described by a set of probabilities $P(i,\, j;\, n)$ for $n > 0$. It is convenient to define the retarded probability function $f_{ij}(n) = P(i,\, j;\, n)\,\theta(n)$, where $\theta(n)$ is a unit step function and $\theta(0) \equiv 1$. These retarded probability functions are equivalent (within a constant factor) to the correlation functions $\langle S_i^z(t) S_j^z(0)\rangle \times \theta(t)$ in the limit of continuous time. The boundary condition is $f_{ij}(n=0) = \delta_{ij}$. This is a consequence of the fact that in the high-temperature limit all pair correlations are zero at $t = 0$ while the autocorrelations have the common value $\langle S_i^z S_i^z \rangle = \frac{1}{3} S(S+1)$.

A system of finite difference equations determines the behavior for discrete time intervals:

$$\begin{aligned} f_{ij}(n) = {} & P_{i+1,\,i} f_{i+1,\,j}(n-1) + P_{i-1,\,i} f_{i-1,\,j}(n-1) \\ & + (1 - P_{i+1,\,i} - P_{i-1,\,i}) f_{ij}(n-1) + \delta_{ij}\delta_{n,0} \;. \end{aligned} \tag{2.2}$$

Equation (2. 2) may be rewritten as a differential equation in the limit of continuous time: We allow $\Delta t \to 0$ but $n\Delta t \to t$. Similarly $P_{ij} \to p_{ij}\Delta t$, where p_{ij} is the hopping probability per unit time. Then

$$\begin{aligned} \frac{\partial f_{ij}(t)}{\partial t} = {} & p_{i+1,\,i}[f_{i+1,\,j}(t) - f_{ij}(t)] \\ & + p_{i-1,\,i}[f_{i-1,\,j}(t) - f_{ij}(t)] + \delta_{ij}\delta(t) \;. \end{aligned} \tag{2.3}$$

We define the Fourier transform of $f_{ij}(t)$ as

$$f(k,\, k',\, \omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} \sum_{l,j} e^{i(k' j - kl)} f_{lj}(t) \;. \tag{2.4}$$

Separating the spatially homogeneous terms from the impurity effects we have

$$\begin{aligned} & [-i\omega + 2p(1 - \cos k)] f(k,\, k',\, \omega) = \delta_{kk'} \\ & \quad + \Delta p\,[f(i=1,\, k',\, \omega)(1 - e^{-ik}) + f(i=-1,\, k',\, \omega) \\ & \quad \times (1 - e^{ik}) - 2f(i=0,\, k',\, \omega)(1 - \cos k)] \;. \end{aligned} \tag{2.5}$$

At this point it is convenient to introduce the Green's functions which describe the pure system ($\Delta p = 0$):

$$G(k,\, \omega) = \frac{1}{-i\omega + 2p(1 - \cos k)} = \sum_s e^{-iks} G(s,\, \omega) \;. \tag{2.6}$$

For small k and ω, $G(k,\, \omega)$ exhibits characteristic diffusive behavior: $G(k,\, \omega) \to i(\omega + ipk^2)^{-1}$. The diffusion constant in this limit is easily identified as p times the square of the lattice constant.

Multiplying Eq. (2.5) through by $G(k,\, \omega)$ and Fourier transforming back to configuration space we have

$$\begin{aligned} f_{lj} = {} & G(l-j) + \tfrac{1}{2}\Delta p \{ [G(l+1) - G(l-1)](f_{1,\,j} - f_{-1,\,j}) \\ & + [G(l+1) + G(l-1) - 2G(l)](2f_{0,\,j} - f_{1,\,j} - f_{-1,\,j}) \} \;, \end{aligned} \tag{2.7}$$

where ω is understood to be an argument of all functions. Equation (2. 7) may be solved within the manifold $l = 0,\ \pm 1$.

After simplification through the use of a recursion relation for the functions $G(s)$,

$$-i\omega G(s) = \delta_{s,0} - p[2G(s) - G(s+1) - G(s-1)] \;, \tag{2.8}$$

we find

$$\begin{aligned} & f_{ij}(\omega) \\ & = G(i-j) - \frac{\Delta p}{2} \left(\frac{[G(i+1) - G(i-1)][G(j+1) - G(j-1)]}{1 + \Delta p/p + (\Delta p/p) i\omega [G(0) + G(1)]} + \frac{[G(i+1) + G(i-1) - 2G(i)][G(j+1) + G(j-1) - 2G(j)]}{1 + \Delta p/p + (\Delta p/p) i\omega [G(0) - G(1)]} \right) . \end{aligned} \tag{2.9}$$

Note that $f_{ij}(\omega)$ is completely symmetric under the interchange $i \leftrightarrow j$. This is indicative of a microreversibility which obtains despite the fact that diffusion is inherently macroirreversible.

Before proceeding further it is worthwhile to derive an explicit expression for $G(s)$ which will be useful in subsequent calculations. Let us choose $s > 0$ and define $z = e^{ik}$ in Eq. (2.6). Then we have

$$G(s) = -\frac{1}{2\pi i} \frac{1}{p} \oint \frac{dz\, z^s}{z^2 - az + 1} \,, \tag{2.10}$$

where $a \equiv 2 - i\omega/p$ and the integration contour is the unit circle. The poles of the integrand occur at $z_\pm = \frac{1}{2}[a \pm (a^2 - 4)^{1/2}]$. Since $z_+ z_- = 1$, only one of these, z_+, lies in the unit circle. Then

$$G(s) = -(1/p) z_+^{|s|} / (z_+ - z_-) \;. \tag{2.11}$$

We have inserted the absolute value sign around s since $G(s)$ is an even function of its argument. For small ω, $G(s)$ exhibits the characteristic $\omega^{-1/2}$ singularity which results in anomalously large magnetic-resonance linewidths: $z_+ - z_- \to 2(-i\omega/p)^{1/2}$ as $\omega \to 0$. Note also that $G(s) = z_+^{|s|}G(0)$, a relation we shall frequently use.

Returning to Eq. (2.9) we consider the case of a nonmagnetic impurity ($\Delta p = -p$). It is easily verified that $f_{ij}(\omega) = 0$ unless i and j are on the same side of the impurity. Hence we specify $i,\ j \geq 1$, and using Eq. (2.11) simplify Eq. (2.9) to

$$f_{ij}(\omega) = G(i-j) + G(i+j-1)\,, \quad i,\ j \geq 1\ . \tag{2.12}$$

This result shows that the impurity acts like a mirror which reflects the spin when it reaches the end of the chain. The first term in Eq. (2.12) represents the direct propagation of the spin from j to i without interference by the impurity, while the second term represents the indirect contribution due to a "reflection" of the spin caused by the presence of the impurity. The $\omega^{-1/2}$ divergence remains essentially unaltered.

B. Single Spin-lattice-Coupled Impurity

The case of a single spin-lattice-coupled impurity may be treated in analogous fashion. For simplicity we assume that the probability of hopping to the left or right is the same for the impurity as for the host atoms, but that there is a loss of spin to the lattice characterized by the phenomenological parameter R. In the case of discrete time intervals this leads to the following probabilities P_{ij}:

$$\begin{aligned} &P_{ij} = 0 \quad \text{if } j \neq i, \quad i \pm 1\,, \\ &P_{i,\,i\pm1} = P\,, \\ &P_{ii} = 1 - 2P - R\delta_{i,0}\,, \end{aligned} \tag{2.13}$$

where $R > 0$ so that the sum of the hopping probabilities for the impurity is less than unity.

The equation analogous to Eq. (2.5) is

$$G^{-1}(k,\ \omega)\, f(k,\ k',\ \omega) = \delta_{kk'} - rf(i=0,\ k',\ \omega)\,, \tag{2.14}$$

where the rate of spin loss is

$$r \equiv \lim_{\Delta t \to 0} \frac{R}{\Delta t}\ .$$

The counterpart to Eq. (2.7) is

$$f_{ij}(\omega) = G(i-j) - rG(i)\, f_{0,j}(\omega) = G(i-j) - \frac{rG(i)G(j)}{1 + rG(0)}\ . \tag{2.15}$$

It is particularly instructive to look at the special case $r/p \to \infty$. This corresponds to the limit in which all the spin which reaches the impurity is absorbed. The parameter r drops out of the problem entirely and the rate of spin loss is determined only by how fast spin diffuses to the impurity:

$$\lim_{r/p \to \infty} f_{ij}(\omega) = \begin{cases} 0\,, & ij \leq 0 \\ G(i-j) - G(i+j)\,, & ij > 0\ . \end{cases} \tag{2.16}$$

The minus sign in Eq. (2.16), in contrast to Eq. (2.12), signals the disappearance of the asymptotic $t^{-1/2}$ behavior in $f_{ij}(t)$. That this is the case may be easily verified since the Fourier transform of Eq. (2.6) gives

$$G(s,\ t) = e^{-2pt} I_{|s|}(2pt)\,, \tag{2.17}$$

where $I_{|s|}$ is a modified Bessel function.[13] Substituting into Eq. (2.16) and using the asymptotic expansion of the Bessel functions[13] we find

$$f_{ij}(t) \to \frac{1}{(4\pi pt)^{1/2}}\, \frac{ij}{pt} + O(t^{-5/2})\ . \tag{2.18}$$

Thus the usual $t^{-1/2}$ asymptotic dependence of the pure chain is replaced by $t^{-3/2}$ for sufficiently large times. The time scale over which Eq. (2.18) is appropriate is clearly determined by the condition

$$(i+j)^2/4pt \ll 1\ ;$$

i.e., the time must be large enough so that the spin would have had significant probability to travel the distance $|i+j|$ in a pure system.

The basic approximation made in Eq. (2.16) was the assumption $|rG(0)| \gg 1$ in the denominator of Eq. (2.15), which may still be justified for finite r/p. For small ω we have $|G(0)| \approx \frac{1}{2}(p\omega)^{-1/2}$, and Eq. (2.16) will be a good approximation for all frequencies $\omega \ll r^2/p$. For a resonance experiment the central line shape is determined by the spectral density of spin fluctuations out to frequencies only of the order of the linewidth. [The corresponding times t in Eq. (1.2) are greater than or of the order of the inverse linewidth.] For such frequencies it is not unrealistic to suggest $\omega \ll r^2/p$ for real materials. For example, the single-ion spin-lattice relaxation rate of Co in $\mathrm{KMnF_3}$ at room temperature has been found[14] to be of the same order of magnitude as p, a few times $10^{12}\ \mathrm{sec}^{-1}$, at least several orders of magnitude larger than typical linewidths. It may be more difficult to find a system for which r is really large compared to p.

III. FINITE IMPURITY CONCENTRATIONS

In considering a real physical system one must deal with finite concentrations of impurities. For nonmagnetic or strongly spin-orbit-coupled impurities, the chain is broken up into dynamically isolated segments. Under these circumstances one need consider only a single segment terminated by two impurities. For simplicity we restrict ourselves to this case.

A. Spin-Orbit Impurities

If we situate the impurities at sites 0 and m, the equation analogous to Eq. (2.15) is

$$f_{ij}(\omega)=G(i-j)-r\left[G(i)f_{0,j}(\omega)+G(m-i)f_{m,j}(\omega)\right]$$
$$=G(i-j)-\frac{r}{2}\left(\frac{[G(i)+G(m-i)][G(j)+G(m-j)]}{1+r[G(0)+G(m)]}+\frac{[G(i)-G(m-i)][G(j)-G(m-j)]}{1+r[G(0)-G(m)]}\right). \tag{3.1}$$

As $m\rightarrow\infty$ this reduces simply to Eq. (2.15). In the limit of large r/p (see the concluding remarks of Sec. II) we get

$$f_{ij}(\omega)=G(i-j)-\frac{[G(i)+G(m-i)][G(j)+G(m-j)]}{2[G(0)+G(m)]}-\frac{[G(i)-G(m-i)][G(j)-G(m-j)]}{2[G(0)-G(m)]}\ . \tag{3.2}$$

To determine the magnetic-resonance line shape we need the Fourier transform $f_{ij}(t)$. We obtain this directly by rewriting Eq. (3.2) in a form which explicitly exhibits its simple pole structure in the ω plane. Using Eq. (2.11) and the fact that $z_+z_-=1$, we have

$$f_{ij}(\omega)=\frac{z_+^m G(0)}{1-z_+^{2m}}\left(z_+^{m-|i-j|}+z_-^{m-|i-j|}-z_+^{m-i-j}-z_-^{m-i-j}\right) \tag{3.3}$$

for $1\leq(i,j)\leq m-1$. From the definitions of $z_\pm$ it is clear that, except for those of $G(0)$, the numerator has no singularities as a function of ω. Note in particular that the bracketed expression in Eq. (3.3) has no square-root branch cuts. The poles of $f_{ij}(\omega)$ occur at $z_+=\exp(n\pi i/m)$, $n=1,\ 2,\ldots,\ 2m$. Equation (3.3) may be manipulated into the form

$$f_{ij}(\omega)=\frac{1}{p}\left(z_+^{m-|i-j|}+z_-^{m-|i-j|}-z_+^{m-i-j}-z_-^{m-i-j}\right)\times\prod_{n=0}^{m}\left[-\frac{i\omega}{p}+2\left(1-\cos\frac{n\pi}{m}\right)\right]^{-1}. \tag{3.4}$$

Thus the only singularities of $f_{ij}(\omega)$ are simple poles at $\omega=-2ip[1-\cos(n\pi/m)]$, and the Fourier transform $f_{ij}(t)$ may be evaluated by the method of residues:

$$f_{ij}(t)=\frac{1}{m}\sum_{n=1}^{m-1}e^{-2pt[1-\cos(n\pi/m)]}\times\left(\cos\frac{n\pi}{m}(i-j)-\cos\frac{n\pi}{m}(i+j)\right). \tag{3.5}$$

The decay is given by a finite sum of exponentials, and is thus more rapid than the power law characteristic of the pure chain.

To recover the pure-chain results we first transform the origin of our coordinates to the center of the chain and then take the limit as $m\rightarrow\infty$, so that the sum over n becomes an integral over wave vector q:

$$f_{ij}(t)\rightarrow\int_{-\pi}^{\pi}\frac{dq}{2\pi}\,e^{-2pt(1-\cos q)}\cos[q(i-j)]$$
$$=e^{-2pt}I_{|i-j|}(2pt)\underset{t\rightarrow\infty}{\rightarrow}(4\pi pt)^{-1/2}\ . \tag{3.6}$$

B. Nonmagnetic Impurities

The general solution for two impurities characterized simply by a different hopping rate Δp is rather complicated and not very enlightening. Thus we consider the limit $\Delta p=-p$ appropriate to nonmagnetic impurities. The equation analogous to Eq. (3.1) is

$$f_{ig}(\omega)=G(i-j)-\frac{p}{2i\omega}\left(\frac{[G(i)-G(i-1)-G(m-i)+G(m-i-1)][G(j)-G(j-1)-G(m-j)+G(m-j-1)]}{[G(0)-G(m-1)]}+\frac{[G(i)-G(i-1)+G(m-i)-G(m-i-1)][G(j)-G(j-1)+G(m-j)-G(m-j-1)]}{[G(0)-G(m-1)]}\right), \tag{3.7}$$

where $1\leq(i,j)\leq m-1$. Equation (3.7) may be cast into a form analogous to Eq. (3.3) in the spin-orbit case:

$$f_{ij}(\omega)=\frac{z_+^{m-1}G(0)}{1-z_+^{2m-2}}\times\left(z_+^{m-1-|i-j|}+z_-^{m-1-|i-j|}+z_+^{m-i-j}+z_-^{m-i-j}\right)\ . \tag{3.8}$$

The singularities in ω of Eq. (3.8) are again simple poles so that the Fourier transform is readily found to be

$$f_{ij}(t)=\frac{1}{m-1}+\frac{1}{m-1}\sum_{n=1}^{m-2}e^{-2pt\{1-\cos[n\pi/(m-1)]\}}\times\left(\cos\frac{n\pi}{m-1}(i-j)+\cos\frac{n\pi}{m-1}(i+j-1)\right), \tag{3.9}$$

where we have explicitly separated out the constant term due to the $\omega=0$ pole.

Physically this term is damped by interactions not included in an isotropic exchange, or hopping, model. However, although it should be damped, it is not spurious. It implies

$$\lim_{t\rightarrow\infty}\langle S_i^z(t)S_j^z(0)\rangle\neq\langle S_i^z\rangle\langle S_j^z\rangle=0\ , \tag{3.10}$$

a factorization usually taken for granted. Such a decoupling is valid here only to order N^{-1} for a chain of N spins. The term arises as a consequence of the fact that the Heisenberg Hamiltonian conserves $S^z\equiv\sum_{i=1}^{N}S_i^z$, the total spin of the system. Thus

$$\langle S^z(t)S_i^z(0)\rangle=\langle S^z(0)S_i^z(0)\rangle=\tfrac{1}{3}S(S+1)\ , \tag{3.11}$$

and the constant term in $\langle S_j^z(t) S_i^z(0)\rangle$, averaged over all j, is $S(S+1)/3N$. Equation (3.9) is consistent with this average value since $f_{ii}(t=0)$ has been normalized to unity.

The correlations we have calculated for pure Heisenberg exchange are damped by an exponential factor $e^{-\eta t}$ due to dipolar interactions, spin-lattice coupling, anisotropic exchange, and interchain coupling. Neglecting variations of these effects along the chain, we can estimate their contributions to the damping rate η by standard perturbation theory:

$$\eta \sim |M|^2/J \,, \tag{3.12}$$

where M is a matrix element characteristic of the interaction and J^{-1} is a measure of the density of final states.

IV. APPLICATION TO NUCLEAR MAGNETIC RESONANCE

One of the most interesting features of the two-spin correlations which have been calculated is their dependence on position in the chain. The most sensitive probe of such position dependence is an NMR experiment, since resonances on different sites relative to impurities may be well resolved. Thus we turn our attention to an analysis of NMR line shapes.

In Eq. (1.2) we have given the standard relation between the relaxation function $\varphi(t)$, which is the Fourier transform of the resonance line shape, and the equilibrium correlation function $\psi(t)$. If the dominant source of line broadening is a hyperfine or electron-nuclear dipole interaction, $H' = \sum A_{ij}^{\alpha\beta} I_i^\alpha S_j^\beta$, where i, j label lattice sites and α, β Cartesian coordinates, then $\psi(t) \propto \sum A_{li}^{\alpha\beta} A_{lj}^{\alpha\beta} \langle S_i^z(t) S_j^z(0)\rangle e^{-iM\omega_0 t}$. We have explicitly extracted the Zeeman time dependence in the final factor $e^{-iM\omega_0 t}$, where $M=0$, ±1 is the appropriate magnetic quantum number. The remaining time dependence in $S_i^z(t)$ is governed by the isotropic exchange Hamiltonian, which allows us to write all the correlation functions in the same form. The two-spin correlation functions in the sum are precisely those we have approximated by $f_{ij}(t)$ in Secs. I–III. To calculate the line shape, we require products of terms of the form

$$\varphi_{ij}(\omega_p, M, t)$$

$$\equiv \exp\left[-\omega_p^2 \int_0^t d\tau\, (t-\tau) \langle S_i^z(\tau) S_j^z(0)\rangle e^{-iM\omega_0\tau}\right], \tag{4.1}$$

where ω_p is a measure of the perturbation strength.

For purposes of later comparison we first consider the ideal infinite chain. There the anomalously large linewidths result from the extremely slow decay of the secular terms ($M=0$) in the relaxation function. For nuclei of magnetic ions we need only $i=j$ in Eq. (4.1) and

$$\varphi_{ii}(\omega_p, M=0, t) \equiv \varphi_{ii}(t)$$

$$= \exp\left[-\left(\frac{\omega_p}{2p}\right)^2 \int_0^y dx\,(y-x)\, e^{-x} I_0(x)\right], \tag{4.2}$$

where we have taken the value of $\psi(x)$ from Eq. (2.17) and $y \equiv 2pt$. The integral in the exponential can be evaluated exactly,[13] with the result

$$\phi_{ii}(t) \xrightarrow[2pt\gg1]{} e^{-(4/3)\omega_p^2 t^2 (4\pi p t)^{-1/2}} = e^{-(\Gamma_0 t)^{3/2}}, \tag{4.3}$$

where $\Gamma_0 \equiv \omega_p |4\omega_p/9\pi p|^{1/3}$ is a measure of the linewidth.

The standard exchange-narrowing theory assumes that the correlation $\psi(\tau)$ decays rapidly enough so that for times larger than $p^{-1}(\sim J^{-1})$ the integral in Eq. (4.1) may be extended to infinity with little resultant error. The simple exponential decay of $\varphi_{ii}(t)$ then implies a Lorentzian line shape. In the present case, however, such an extension is not permissible because of the slow $(\sim \tau^{-1/2})$ decay of $\psi(\tau)$. This results in the anomalous $t^{3/2}$ exponent of Eq. (4.3). We also point out that the three-dimensional exchange-narrowed linewidth is of order $\omega_p(\omega_p/p)$, whereas the narrowing factor in one dimension is seen to be only $(\omega_p/p)^{1/3}$; NMR lines are much broader in one dimension.

Now consider a chain terminated by spin-lattice-coupled impurities. Then $f_{ij}(t)$ is given by Eq. (3.5), and the secular contribution to the relaxation function is

$$\varphi_{ij}(t) = \exp\left(-\frac{\omega_p^2}{m} \sum_{n=1}^{m-1} (x_n t + e^{-x_n t} - 1)\right),$$

$$\times \frac{\cos[n\pi(i-j)/m] - \cos[n\pi(i+j)/m]}{x_n^2} \tag{4.4}$$

where $x_n \equiv 2p[1-\cos(n\pi/m)]$. It is convenient to extract from the exponent the term linear in t and to examine the circumstances under which this term is dominant. Rather than do the sums over n in Eq. (4.4) explicitly we note that only the linear time dependence remains if the integral over τ in Eq. (4.1) is extended to infinity. Hence to calculate the coefficient of t in Eq. (4.4) we need only evaluate the Fourier transform $f_{ij}(\omega=0)$, which from Eq. (3.3) is

$$f_{ij}(\omega=0) = (1/4pm)\,[2m(|i+j| - |i-j|) - 4ij]. \tag{4.5}$$

Then Eq. (4.4) becomes

$$\varphi_{ij}(t) = \exp\left[-\omega_p^2 f_{ij}(\omega=0)\, t - \frac{\omega_p^2}{m} \times \sum_{n=1}^{m-1}\left(\cos\frac{n\pi(i-j)}{m} - \cos\frac{n\pi(i+j)}{m}\right)\frac{(e^{-x_n t}-1)}{x_n^2}\right], \tag{4.6}$$

and $\varphi_{ij}(t)$ is the product of a simple exponential term and a correction factor due to the finite upper limit in the integral (4.1). At small times this correction term ensures that the exponent in Eq. (4.6) is quadratic in t. However, at times greater than the inverse linewidth, the correction may be neglected for sufficiently short chains. This will certainly be true if the sum of decaying exponentials in Eq. (4.6) damps in a time significantly shorter than $\varphi_{ij}(t)$ itself. In an infinite pure chain the relaxation of the exponentials becomes increasingly slow at small wave vectors so that the simple exponential decay of $\varphi_{ij}(t)$ is never realized. But if the chain is short enough, the lower limit on allowed wave vectors makes the relaxation sufficiently rapid for the simple exponential form to be a good approximation.

From Eq. (4.4) we see that only the linear term in t will be important if for all n we have

$$\frac{\omega_p^2}{m}\,\frac{\cos[n\pi(i-j)/m]-\cos[n\pi(i+j)/m]}{x_n^2} \ll 1. \tag{4.7}$$

The most stringent condition arises for $n=1$. Then near the center of the chain the difference of cosines is approximately 2, $1-\cos(\pi/m)\approx\frac{1}{2}(\pi/m)^2$, and a condition on chain length which permits the neglect of the correction terms is

$$m^3 \ll p^2\pi^4/2\omega_p^2. \tag{4.8}$$

For the reasonable ratio $\omega_p/p \sim A/J \lesssim 10^{-2}$, when ω_p corresponds to a contact hyperfine interaction, the length is thus restricted to $m \ll 100$. If this condition is satisfied, the line profile can be expected to be predominantly Lorentzian. For transferred hyperfine or dipolar interactions ω_p/p will be much smaller and the restriction on chain length correspondingly less severe.

In practice one hopes to isolate the resonances of nuclei near an impurity. In that case even the condition (4.8) is unnecessarily restrictive. If i and j are close to an impurity, even for m large, one can show by transforming the sum in Eq. (4.6) to an integral that the ratio of the correction term to the leading term is $\sim(pt)^{-1/2}$. This is negligible for all times of interest as anticipated on physical grounds. Thus a Lorentzian line shape is to be universally expected for resonance near an impurity.

To summarize, under the conditions on m, i, and j outlined above, the correction terms in Eq. (4.6) have a negligible effect so that $\varphi_{ij}(t)$ decays as a pure exponential

$$\varphi_{ij}(t) \approx e^{-\Gamma_{ij}t}, \tag{4.9}$$

where

$$\Gamma_{ij} = (\omega_p^2/4pm)(2m|i+j| - 2m|i-j| - 4ij). \tag{4.10}$$

For the case of resonance on the nucleus of a magnetic ion only the autocorrelation functions $\varphi_{ii}(t)$ are required. From Eq. (4.10) the linewidth $\Gamma_{ii}=\omega_p^2\, i(m-i)/pm$ is then strongly dependent on position in the chain, increasing linearly with distance from the nearest impurity if $i \ll m$.

Resonance widths near an impurity are also significantly smaller than those in a pure chain. The ratio of the impure to pure linewidths is

$$\frac{\Gamma_{ii}}{\Gamma_0} = \left(\frac{3(\pi)^{1/2}\omega_p}{2p}\right)^{2/3} \frac{i(m-i)}{m}\ . \tag{4.11}$$

Again taking $\omega_p/p = 10^{-2}$ we have $\Gamma_{ii}/\Gamma_0 \approx 0.13\, i(m-i)/m$. Thus, for example, the nearest neighbor to an impurity should have a width approxitely 8 times smaller than that characteristic of the pure chain. For larger i, when the ratio (4.11) becomes of order unity, our approximation fails and the correction terms in (4.6) are no longer negligible. At this point the line shape also begins to look more like the pure case. In fact, the condition $\Gamma_{ii}/\Gamma_0 \ll 1$ restricts the chain length approximately as does Eq. (4.8).

For the case of resonance on the nucleus of a nonmagnetic ion (transferred hyperfine or dipolar interaction) both the auto and pair relaxation functions are required to compute the line shape. If we take the simplest possible case where the nucleus is coupled with equal strength ω_p' to two magnetic ions on sites i and $i+1$, the Lorenzian linewidth is

$$\begin{aligned}\Gamma &= \Gamma_{ii} + \Gamma_{i+1,i+1} + 2\Gamma_{i,i+1}\\ &= (\omega_p'^2/mp)[m(4i+1)-(2i+1)^2]. \end{aligned}\tag{4.12}$$

If $i/m \ll 1$, Γ again has a linear dependence on distance from the nearest impurity. As before, the linewidths near an impurity are strongly narrowed, by perhaps 2–3 orders of magnitude, when compared to the pure case.

For a chain terminated with nonmagnetic impurities one can show that under any conditions the calculated NMR linewidths must be greater than those in a pure system. This is perhaps physically obvious since only a finite number of lattice sites are available on which to distribute spin information. Mathematically such an assertion is equivalent to proving that $f_{ij}(t) > G(i-j, t)$ for all t, since then the integral in the exponent of the relaxation function [Eq. (4.1)] is always greater than its counterpart in the pure case. We rewrite Eq. (3.8) in the form

$$\begin{aligned} f_{ij}(\omega) - G(i-j) &= G(i+j-1) + \frac{G(0)z_+^{2m-2}}{1-z_+^{2m-2}}\left(z_+^{|i-j|} + z_-^{|i-j|} + z_+^{|i+j-1|} + z_-^{|i+j-1|}\right)\\ &= G(i+j-1) + \sum_{n=1}^{\infty}\left[G(2n(m-1)-|i-j|) + G(2n(m-1)+|i-j|) + G(2n(m-1)-|i+j-1|)\right. \end{aligned}$$

$$+G(2n(m-1)+|i+j-1|)] \;, \qquad (4.13)$$

where we have expanded $(1-z_+^{2m-2})^{-1}$ as a geometric series since z_+ always lies within the unit circle. A Fourier transform of Eq. (4.13) in ω then immediately proves the assertion, since the $G(s,t)$ are positive definite probabilities for all time. Note further that this result is also independent of the extra damping due to dipolar or other interactions, since these would simply lead to multiplication of the Fourier transform of Eq. (4.13) by an over-all exponential factor.

The relaxation functions for the chain terminated by nonmagnetic impurities may be analyzed in the same manner as the spin-lattice case, but with the proviso that care be taken with the pole of $f_{ij}(\omega)$ near $\omega=0$. Explicitly including the damping of the spin correlations due to perturbations such as dipolar interactions, we find for the secular contribution to the relaxation function

$$\varphi_{ij}(t)=\exp\left(-\frac{\omega_p^2}{m-1}\sum_{n=0}^{m-2}\frac{\cos[n\pi(i-j)/(m-1)]+\cos[n\pi(i+j-1)/(m-1)]-\delta_{n,0}}{(\eta+y_n)^2}\,[(\eta+y_n)t+e^{-(\eta+y_n)t}-1]\right) \;, \qquad (4.14)$$

where $y_n\equiv 2p[1-\cos(n\pi/m-1)]$. Here η is the additional rate of damping which is to be estimated from Eq. (3.12). When this rate of damping is small, approximately the same restriction on chain length as found for the spin-lattice case [Eq. (4.8)] applies, if the correction terms (other than $n=0$) in Eq. (4.14) are to be dropped. However, in contrast to the case of spin-lattice-coupled impurities, spin information tends to be dissipated more slowly near the chain ends, and the most severe limitations on length occur there.

For the terms $n\neq 0$ in Eq. (4.14) we see that η may be neglected if $\eta\ll y_n$. If the damping arises principally from anisotropic exchange we have from Eq. (3.12) that

$$\eta\approx(\Delta J/J)^2 J \;, \qquad (4.15)$$

where $\Delta J/J$ is the percentage anisotropy. Thus even an anisotropy of 3% yields $\eta\approx 10^{-3}J$. Similarly, for dipolar damping,

$$\eta\approx(\mu_B^2/a^3J)^2 J \;, \qquad (4.16)$$

where μ_B is the Bohr magneton and a is the separation between magnetic lattice sites. For the conservative estimates, $a=3$ Å and $J=5$ °K, we have $\eta\approx 10^{-4}J$. The damping due to spin-lattice coupling is similarly expected to be very small. With these estimates it is not difficult to show that in fact $\eta\ll y_n$ in Eq. (4.14), for all $n\neq 0$ when the chain is short enough so that Eq. (4.8) is satisfied.

In the term with $n=0$, the relevant comparison is the size of η compared with the decay rate β_{ij} of $\varphi_{ij}(t)$ itself. Since we have already shown that $\beta_{ii}>\Gamma_0$,

$$\frac{\eta}{\beta_{ii}}<\frac{\eta}{\Gamma_0}\approx\left(\frac{|M|}{J}\right)^2\left(\frac{J}{\omega_p}\right)^{4/3} \;, \qquad (4.17)$$

where M is a matrix element characteristic of the perturbation Hamiltonian which we have estimated in Eqs. (4.15) and (4.16). For an assumed hyperfine coupling strength $\omega_p/J\approx 10^{-2}$ and estimating $(|M|/J)^2\approx 10^{-4}$ we have

$$\eta/\beta_{ii}<10^{-4/3} \;. \qquad (4.18)$$

Under these conditions the $n=0$ term in Eq. (4.14) gives rise to a Gaussian time dependence independent of η and

$$\varphi_{ij}(t)=e^{-(\alpha t^2+\Gamma_{ij}t)} \;, \qquad (4.19)$$

where $\alpha\equiv\omega_p^2/2(m-1)$ and Γ_{ij} may be identified as the constant term in the expansion of Eq. (3.8) about $\omega=0$:

$$\Gamma_{ij}=[\omega_p^2/4p(m-1)][(m-1-|i-j|)^2+(m-|i+j|)^2+\tfrac{1}{3}m(m-2)-(m-1)^2] \;. \qquad (4.20)$$

When ω_p/J is very small or η is quite large so that $\eta/\beta_{ii}\gg 1$ [c.f. Eq. (4.17)], conventional exchange-narrowing theory becomes applicable. The relaxation function is then pure Lorentzian having a width

$$\beta_{ij}=\omega_p^2\int_0^\infty e^{-\eta\tau}f_{ij}(\tau)\,d\tau=\omega_p^2 f_{ij}\;\;(\omega=i\eta) \;. \qquad (4.21)$$

Here $f_{ij}(\omega=i\eta)$ is the correlation function calculated from the isotropic exchange Hamiltonian only [Eq. (3.9)].

For resonance on a magnetic ion at site i when η is negligible Eq. (4.19) is applicable with

$$\Gamma_{ii}=[\omega_p^2/4p(m-1)][(m-2i)^2+\tfrac{1}{3}m(m-2)] \;. \qquad (4.22)$$

In contrast to the chain terminated by spin-lattice-coupled impurities, this function has no pronounced position dependence for small i. It is also clear that the width of the resonance is greatest in the vicinity of an impurity and smallest near the chain center. Equation (4.19) predicts the line profile to be Gaussian near the center and Lorentzian in the wings.

For the case of resonance on a nonmagnetic ion between two spin sites the analysis and results are similar. There is again no strong dependence of the resonance width on distance from an impurity other than through a purely geometrical effect. For a nucleus next to an impurity only one nearest neighbor plays a role in the relaxation, and the resonance is significantly narrowed.

We close this section by exploring the experimental observability of these effects. Although impurity NMR lines have been studied in some detail in three-dimensional systems, linewidths in one-dimensional materials with similar physical parameters (exchange strengths, spins, lattice constants) are characteristically much larger, as we have previously pointed out. This is a consequence of the relative importance of small wave vectors in one dimension and the associated enhanced strength of the spectral weight of spin fluctuations at low frequencies, which control the NMR linewidth.

We compare the main NMR linewidth (for nuclei far from an impurity) with the resonance frequency shift near an impurity. As an estimate of the shifts to be expected we consider the simple example of a nonmagnetic impurity and a nucleus between the impurity and its nearest neighbor. Characterizing the nucleus-electron interaction, as above, by a strength ω_p' we estimate the resonance shift by $\Delta\omega \approx \omega_p' \langle S_1^z \rangle$. Then the ratio of the shift $\Delta\omega$ to the pure linewidth Γ_0 [see Eq. (4.3)] is

$$\Delta\omega/\Gamma_0 \approx (\tfrac{9}{4}\pi)^{1/3}(p/\omega_p')^{1/3}\langle S^z \rangle \ , \tag{4.23}$$

which is typically of order unity for polarizations of a few percent, readily obtained even at the high temperatures for which our theory is valid.

A more favorable case is found with spin-lattice-coupled impurities. For sufficiently high impurity concentrations we have seen that the main resonance may be considerably narrower than Γ_0, and linewidths near the impurities are smaller still [see Eq. (4.11)]. The shifts may still be of the order of $\omega_p' \langle S_1^z \rangle$, due to the different spin magnitude of the impurity, for example. We now compare $\Delta\omega$ with an *average* linewidth for the chain of m atoms as determined from Eq. (4.12):

$$\Delta\omega/\Gamma_{\mathrm{av}} \approx 3(p/\omega_p')\langle S^z \rangle /2m. \tag{4.24}$$

For $m \approx 20$ and $(p/\omega_p') \approx 10^3$, this suggests that the lines will be resolved if $\langle S^z \rangle \gtrsim 10^{-2}$. There will be a smaller shift for the nuclei at other positions along the chain, since the altered molecular field of the impurity will lead to a variation in $\langle S_i^z \rangle$ along the chain. The effect is, of course, largest at the neighbor of the impurity, where the correction to the local susceptibility is of order T_N/T, if T_N is the mean-field Néel temperature. The EPR experiments on one-dimensional systems imply that the high-temperature limit for spin dynamics is realized at least by $T = 5T_N$. At this temperature the ratio (4.24), for a nucleus between the first and second neighbors to an impurity, is reduced by a factor of order $T_N/T \approx 0.2$, and this additional line should still be resolved for $\langle S^z \rangle \gtrsim 0.05$. For typical values of T_N of a few tens of degrees, standard laboratory fields should then be sufficient.

V. CONCLUSION

The simple hopping model for the high-temperature spin dynamics of a linear chain has, as anticipated, demonstrated important modifications in local spin dynamics due to impurities. Although these will be manifested in such bulk properties as the susceptibility $\chi(q, \omega)$, we have concentrated on the interesting variations in local behavior near an impurity which might be observed in nuclear-resonance experiments, as discussed in Sec. IV. We have studied two-spin correlation functions, which may determine the resonance line shape through relaxation functions of the form (4.1). The $e^{-(\Gamma_0 t)^{3/2}}$ dependence of the relaxation function characteristic of the pure chain is a direct consequence of the long time persistence ($\sim t^{-1/2}$) of spin correlations associated with diffusion in one dimension. When the diffusion is inhibited, as by appropriate impurities, one expects a return to the simple exponential form $e^{-\Gamma t}$ of standard exchange-narrowed systems, corresponding to a Lorentzian resonance line shape. In fact, for a nucleus close to a strongly spin-lattice-coupled impurity (where spin information is lost readily to the lattice rather than continuing to diffuse along the chain), we find this is precisely what occurs. Furthermore, if the separation between impurities is sufficiently small [see Eq. (4.8)], then the exponential decay is found for all positions along the chain. The dependence of the decay rate Γ_{ij} on the positions i and j of the two spins is given by Eq. (4.11); the magnetic nucleus linewidth Γ_{ii} increases linearly with distance from the nearest impurity. The smallest linewidth, associated with the neighbor to an impurity, may be typically one to three orders of magnitude smaller than the linewidth appropriate to the pure chain, depending on the source of the line broadening.

It has been shown that nonmagnetic impurities always lead to broader NMR linewidths than those found for the pure chain. Physically the impurities prevent loss of spin information from finite chain segments, decay of the spin correlation functions occurs more slowly, and the relaxation function $\varphi_{ij}(t)$ is damped more rapidly. The decay of the uniform ($q = 0$) spin density on the segment must be treated separately, and it contributes a Gaussian factor to the otherwise exponential relaxation function [see Eq. (4.19)]. The restriction on the length of the segment for this description to be valid is approximately the same as for the spin-lattice-coupled impurities.

Finally, we have investigated the probable observability of these effects. We have found that, if NMR can be seen in the pure chain, it is likely that lines due to first and perhaps second neighbors to an impurity can be isolated from the main resonance and observed, using reasonable magnetic fields. The most favorable circumstances are associated with (i) strongly spin-lattice-coupled impurities at relatively high concentrations, (ii) resonant nuclei of nonmagnetic atoms, and (iii) the weakest possible broadening mechanism (e.g., electron-nuclear dipole interactions).

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Calculation of the Phonon Sideband of the *R* Line in MgO:Cr^{3+}

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A calculation of the phonon sideband associated with the $^2E_g \rightarrow {}^4A_{2g}$ transition of a Cr^{3+} ion at a cubic site in MgO is presented. The short-range coupling model used and the method of calculation follow closely those used in a previous calculation of the sidebands for MgO : V^{2+} and MgO : Ni^{2+}. Satisfactory agreement with experiment is obtained by assuming that only displacements of the impurity ion and its nearest neighbors are coupled to the electronic transition. Differences between the coupling for the Cr^{3+} ion and that for the divalent ions are discussed as is the validity of the assumption of short-range coupling.

I. INTRODUCTION

There has been considerable experimental interest in the fluorescence spectrum of Cr^{3+} in MgO. A useful review of work done up to 1962 has been given by Schawlow.[1] The spectrum consists of a sharp line at 14 319 cm^{-1} (the *R* line) accompanied by weaker satellite sharp lines (the *N* lines) at lower energies and an attendant phonon sideband. The intensities of the satellite lines are found to depend strongly on the method of preparation in a way which Schawlow *et al.*[2] have shown to be consistent with the satellites arising from local charge-compensation effects. The symmetries of the complexes formed when Cr^{3+} substitutes for a Mg^{2+} lattice ion have been established by electron spin resonance (ESR) experiments.[3,4] The most abundant pattern in the ESR spectrum is isotropic and consistent with the Cr^{3+} ion being at a site of cubic symmetry. From Zeeman-splitting experiments on the *R* line, Sugano *et al.*[5] have established that the electronic transition is magnetic dipole from a ^2E_g excited state to the $^4A_{2g}$ ground state. By examining a range of crystals prepared in different ways to give different intensities of the *R* and *N* lines, Imbusch[6] has identified the part of the sideband which is due to the *R* line, that is the part which accompanies electronic transitions in Cr^{3+} at cubic sites. This experimental sideband is reproduced as the continuous line in Fig. 1(a) and is in good agreement with results published by Glass and Searle.[7]

Recently, Sangster and McCombie[8] (this paper