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Short Range Order Effects on NMR Linewidths in Paramagnets*

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The theory of Moriya for the temperature dependence of the exchange narrowed-hyperfine broadened NMR linewidths in paramagnets is reformulated so as to include the effects of short range order. A comparison is made between the present work and the Hubbard correlation function theory, as well as with our own experiments on the F^{19} NMR in MnF_2 and $KMnF_3$ in the paramagnetic region. In both instances the results are most satisfactory.

A teoria de Moriya sobre a dependência com a temperatura da largura de linha NMR alargada por interação hiperfina e estreitada por interação de troca é reformulada de maneira a incluir os efeitos da ordem de curto alcance. Os resultados obtidos são comparados com os da teoria da função de correlação de Hubbard bem como com nossos resultados experimentais de NMR do F^{19} em MnF_2 e $KMnF_3$ na fase paramagnética. Em ambos os casos se obtém boa concordância.

1. Introduction

In three basic papers[1,2,3], Moriya laid the groundwork for much of our understanding of the relaxation and linewidth phenomena encountered in nuclear magnetic resonance (NMR) of magnetic insulators, both above and below the ordering temperature T_c (Ref. 4). There have been a succession of refinements and developments of his theories[5] and extensive comparisons made with experimental results[6].

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Briefly summarized, the situation with respect to theory and experiment is as follows:

i) Below T_c, where the excitations of the spin system are well defined (spin waves), the observe. linewidths[7] and relaxation rates[S] are now in excellent agreement with the spin wave scattering theory predictions;

ii) At temperature $T \gg T_c$, the magnitude of the observed widths[9] correspond reasonably well to the high temperature correlation function theoretical predictions[10];

iii) In the immediate vicinity of T_c i.e., ($|T_c - T| \ll T_c$), the critical-like divergent behavior of the relaxation rates and linewidths, observed[11] and predicted[3], are in qualitative accord. However, the measured temperature dependence to the NMR linewidths through most of the paramagnetic region has been given limited theoretical attention and hence is only qualitatively understood. Since the form of the interactions between the nuclear moment and the electronic magnetization are well known, it is clear that the problems in the intermediate temperature region are a direct consequence of the theoretical difficulties experienced in treating the spin dynamics of a many-bodied system in the paramagnetic regime.

It is our intent here to provide an extension of the theory originally developed by Moriya for treating the critical region, in which we now include the effects of short range order. To do so we utilize the concept of the "reaction field"[12,13] to calculate the dynamic susceptibility. The theory of Mori and Kawasaki[14] is employed to obtain the time evolution of the spin correlation functions. In this regard our work represents a refinement over the treatment of Maarschall[15], who first recognized the importance of the reaction field to the linewidth problem, but made a crude approximation for the spin dynamics.

As an application of the theory, we compare our experiments on the linewidth of the F^{19} NMR in MnF_2 and $KMnF_3$ with the extended theory. The resulting improved agreement between theory and experiment indicates the importance of pair correlations in determining relaxation rates and linewidths of nuclei in paramagnets.

Finally, we are able to make a favorable comparison between our reaction field-corrected Moriya theory and Hubbard's more sophisticated, but also more complex and less transparent, calculation of the dynamic behavior of the spin-correlation functions.

2. Summary of Moriya's Linewidth Theory

In this section we give a brief summary of those parts of Moriya's theory of the NMR linewidth that are relevant to calculations in the paramagnetic phase. The broadening of NMR lines has its origin in the interactions between the nucleus and its environment. These interactions may be classified in the following three categories:

1) Hyperfine and electronic dipolar interactions (nuclear spin-electron spin) modulated by the exchange and other interactions between the electron spins and by the lattice vibrations[1,2],

2) Indirect nuclear spin interaction via the hyperfine interaction[16,17,3],

3) Nuclear dipole-dipole interaction and other mechanisms in which the electron spin does not take part[18].

Since the intent of this paper is to explore the effect that short range order has on the spin dynamics of a paramagnet as manifest in its contributions to the NMR linewidth and relaxation rates, we will confine ourselves to the first category given above. Then the Hamiltonian describing interactions between the resonant nucleus and neighboring magnetic ions can be written in the form

$$H_{\text{int}} = \sum_j I . \overleftrightarrow{F}_j . S_j \tag{1}$$

characterized by the interaction tensors $\overleftrightarrow{F}_j$, to be specified in each particular case. In terms of these, the nuclear spin-lattice relaxation rate $1/T_1$ is given immediately by the Fermi Golden Rule as

$$\frac{1}{T_1} = \frac{1}{2} h^{-2} \int_{-\infty}^{+\infty} dt \cos(\omega_o t) \sum_{j,j',\nu,\nu'} (F_j^{x\nu} + i F_j^{y\nu}) (F_{j'}^{x\nu'} - i F_{j'}^{y\nu'}) \cdot \cdot \langle \{ \delta S_j^{\nu}(t) \, \delta S_{j'}^{\nu'}(0) \} \rangle , \tag{2}$$

where ω_o is the nuclear resonance frequency, v and v′ are summed over x, y and z, $\delta A \equiv A - (A)$, ( ) denotes an equilibrium thermal average, and $\{AB\} = (AB + BA)/2$. The Fourier transform just provides the usual energy-conserving δ-function (in this case initial and final electronic states differ by the energy ω_o associated with a nuclear spin flip) and the remaining factors are the squares of the appropriate matrix elements of H_{int}. Only

F^{xv} and F^{Yv} appear in H,,, with the operators I^x and I^y which can flip a nuclear spin, transfering energy to the lattice, and F^{zv} therefore does not appear in Eq. (2) for $1/T_1$.

The nuclear lineshape $I(\omega)$ can also be expressed in terms of the electron spin correlation functions appearing in Eq. *(2)*. As $I(\omega)$ gives absorption of energy by the nuclei from an electromagnetic field of frequency *w*, it is essentially the imaginary part of the transverse nuclear magnetic susceptibility at frequency ω, related in turn by the fluctuation-dissipationtheorem to the nuclear spin correlation function $\int dt\, \langle \tilde{I}^{+}(t) \tilde{I}^{-}(0) \rangle$ exp *(icot)*. Here the tilde indicates that the time dependence of $\tilde{I}^{+}(t)$ is governed by the *full* Hamiltonian, including H_{int}. If this latter dependence is treated in the interaction picture, then, within an approximation on the character of the electronic spin fluctuations valid under rather general conditions, one can write $I(\omega)$ in the form

$$I(\omega) = \int dt \; \exp\,[i(\omega - \omega_0)t - \Psi(t)], \tag{3}$$

where

$$\Psi(t) = h^{-2} \int_0^t d\tau\,(t-\tau) \sum_{j,j'} \sum_{v,v'} \Big\{ F_j^{zv} F_{j'}^{z\,v'} + \frac{1}{2}\, e^{i\omega_0 \tau} \times$$
$$x\; (F_j^{xv} + i F_j^{yv})(F_{j'}^{x\,v'} - i F_{j'}^{yv'}) \Big\} ((6 S_j^{v}(\tau)\, \delta S_{j'}^{v'}(0)\}\rangle\,, \tag{4}$$

where the time dependence of the operators $S(t)$ is now governed by a Hamiltonian *without* H_{int}. The corrections to Eq. *(4)* involve cumulant averages of higher order (than second) in H_{int}.

The calculation of $1/T_1$ and of $I(\omega)$ has then been essentially reduced to the determination of various electronic two-spin correlation functions. The expressions *(2)* and *(4)* are valid in both magnetically ordered and paramagnetic phases. We will be concerned here only with the latter case and we can therefore replace δS_j by S_j in all expressions.

If the electron spin correlation functions decay sufficiently rapidly, we can characterize $I(\omega)$ by a single parameter, the transverse relaxation time T_2. First, we specify the decay rate in terms of a correlation time τ_c, defined as

$$\tau_c = \int_0^\infty dt \, \langle\{S_j^y(t)\, S_j^y(0)\}\rangle / \langle[S_j^y(0)]^2\rangle \cdot \tag{5}$$

The values of time t important in Eq. (3) are of the order of Δ^{-1}, where A is the linewidth of $I(\omega)$, whereas the important values of τ in Eq. (4) are of the order of τ_c. Thus, when $\tau_c \ll \Delta^{-1}$, τ may be neglected in the factor $(t-\tau)$ of Eq. (4) and the upper limit of τ integration extended to ∞ for all t of interest. This approximation gives $\Psi(t)$ linear in t:

$$\Psi(t) \approx t/T_2$$

or

$$\langle I^+(t)\, I^-(0)\rangle \propto e^{-t/T_2}, \tag{6}$$

where the second form results from the above association of $I(\omega)$ with the transverse nuclear susceptibility. Then $I(\omega)$ is the Fourier transform of $\exp(-t/T_2)$, i.e., a Lorentzian of width $\mathbf{A} = 1/T_2$. At short times $t \sim \sim \tau_c \ll T_2$, the approximation giving the exponential of Eq. (6) breaks down; correspondingly, the Lorentzian for $I(\omega)$ is cut off at large o, $\mathbf{o} \gg$ A $= 1/T_2$. Since the frequency moments of $I(\omega)$ are finite, whereas those moments diverge for a Lorentzian, the cutoff is essential, but the results are relatively insensitive to its precise form.

Having demonstrated the essential role played in the calculation of both nuclear spin-lattice relaxation rates and NMR linewidths by electronic twospin correlation functions, we devote the remainder of this section to a discussion of these functions. It is convenient to work with the collective spin operators

$$S, = N^{-1/2} \sum_j \boldsymbol{S}_j \exp(\mathrm{i}q.\boldsymbol{R}_j) \tag{7}$$

and the corresponding correlation functions $\langle\{S_q^\nu(t)\, S_{-q}^{\nu'}\}\rangle$ (all others, $\langle S_q S_{q'}\rangle$ with $q' \neq -q$, vanish by translational invariance of the lattice). We can conveniently separate the thermodynamic and dynamic features of the behavior of these functions by rewriting them in terms of the corresponding "relaxation functions", defined by

$$(A(t),\ B(0)) \equiv \int_0^\beta d\lambda \, \langle A(t - i\lambda)\, B(0)\rangle, \tag{8}$$

where $\beta = (k_B T)^{-1}$. This is simply related to the ordinary correlation function[19] by

$$\int \mathrm{d}t\, e^{i\omega t} \langle A(t)\, B(0) \rangle = \frac{1}{2} \hbar\omega \coth (\beta\hbar\omega/2)\, (A(t), B(0))_\omega \tag{9}$$

where the subscript on the last term denotes the Fourier transform of that relaxation function at frequency ω. The function $(A(t), B(0))_\omega$ describes the response in a system of the observable A to an external field coupled to B at frequency ω, that relation just being a statement of the fluctuation-dissipation theorem. In particular, for the spin operator of interest here, we have the static wavevector dependent susceptibility $\chi(q)$ given as

$$\chi_{\nu\nu'}(q) = (S^{\nu}_{q}(0),\ S^{\nu'}_{-q}(0)). \tag{10}$$

For a magnetically isotropic system $\chi_{\nu\nu'}(q) = \delta_{\nu\nu'}\ \chi(q)$, an approximation we will use, consistent with the choice of a Heisenberg Hamiltonian to describe interactions between the electronic spins Furthermore for the frequencies ($\omega = \omega_0$) and temperatures ($T > T_c$) of interest in the present work, we can take $\coth (\beta\hbar\omega/2) \approx 2/(\beta\hbar\omega)$, so that we can write

$$\langle \{ S^z_q(t)\, S^z_{-q}(0) \} \rangle = k_B\, T\chi(q) f_q(t), \tag{11}$$

where

$$f_q(t) \equiv \frac{(S^z_q(t),\ S^z_{-q}(0))}{(S^z_q(0),\ S^z_{-q}(0))}. \tag{12}$$

Thus the thermodynamic variation of the correlation functions have been isolated primarily in the factor $T\chi(q)$; the normalized function $f_q(t)$ expresses essentially the dynamical features, and now one can make suitable separate approximations for these two factors.

For $\chi(q)$ Moriya uses the Weiss molecular field approximation (MFA)

$$\chi(q) \sim \frac{\chi_0}{1 - \chi_0 J(q)} \tag{13}$$

where χ_0, the "bare" susceptibility per atom (i.e., the susceptibility of a non-interacting spin), is given by the Curie law

$$\chi_0 = \beta S(S + 1)/3. \tag{14}$$

The exchange interactions between spins are described by

$$J(q) = \sum_j J_{jj'} \exp \left[i\, \boldsymbol{q}.(\boldsymbol{R}_j - \boldsymbol{R}_{j'}) \right], \tag{15}$$

where the $J_{jj'}$ are the standard exchange constants of a Heisenberg Hamiltonian

$$H_{,,} = -\frac{1}{2}\sum_{jj'} J_{jj'}\, \mathbf{S}_j . \mathbf{S}_{j'} \, . \tag{16}$$

For the dynamical function $f_q(t)$, Moriya makes use of a technique suggested by Mori and Kawasaki[14]. The idea is to write $f_q(t)$ in terms of the relaxation function of the torques $\dot{S}_q(t)$:

$$f_q(t) = 1 - \int_0^t d\tau\, (t-\tau)\, (\dot{S}^z_q(\tau),\ \dot{S}^z_{-q}(0))/(S^z_q(0),\ S^z_{-q}(0)), \tag{17}$$

a mathematical identity since $f_q(0) = 1$ and $\dot{f}_q(0) = 0$.'' If the correlation between torques decays much faster than that between spins, i.e., if the important times in Eq. (17) for which $(\dot{S}^z_q(t), \dot{S}^z_{-q}(0))$ is appreciable are much smaller than the characteristic times t for which $f_q(t)$ is large, then Eq. (17) can be approximated by

$$f_q(t) \approx f_q(0)\ \exp\ (-\Gamma_q t), \tag{18}$$

with

$$\Gamma_q = \int_0^\infty dt\ (\dot{S}^z_q(t),\ \dot{S}^z_{-q}(0))/(S^z_q(0),\ S^z_{-q}(0)), \tag{19}$$

where the argument follows precisely the same lines as that leading to Eq. (6). That this is the case for small q follows from the fact that for the pure Heisenberg Hamiltonian S^z_q for q = 0 is a conserved quantity, which therefore never decays, and by continuity $f_q(t)$ decays slowly for small q, whereas there is no such conservation law for $\dot{S}_q$. In general, for larger q, there is no similar disparity in decay times. However, in the critical region $(T-T_c)/T_c \ll 1$, where Moriya originally applied this theory to nuclear relaxation[3], the approximation can be justified as follows. The susceptibility $\chi(q)$ diverges at T_c for $q = K_0$, and this implies particularly large amplitude fluctuations for $q \approx K_0$ and $|T-T_c|/T_c \ll 1$. At the same time, there is critical slowing down of these fluctuations, and both effects imply a dominant contribution from wave vectors q near K_0 to the low frequency fluctuations which determine T_1 and T_2. Again, no similar slowing down is expected[20] for the torques $\dot{S}_q(t)$ near $q = K_0$, and the torque correlation functions will therefore decay much more rapidly than $f_q(t)$ for these dominantly important values of q. For other values of q and of T, we make use of the fact that we require only $f_q(\omega)$ for $\omega \approx 0$ to determine T_1 and T_2. Since $f_q(t = 0)$ is by definition normalized to unity, $f_q(\omega \approx 0)$ is set by the decay rate of $f_q(t)$, whether that function is exponential (as in Eq. (18)) or not. From Eq. (17), we see that the decay rate is *approximately* given by Eq. (19), whether or not $\dot{S}_q(t)$ decays much faster than $S_q(t)$ (note: it never decays slower than $S_q(t)$). Therefore, we continue to use the result (19) for all q and all temperatures[21]. Because of the integral nature of the relation (19), the only important feature of the time dependence of $(\dot{S}^z_q(t), \dot{S}^z_{-q}(0))$ which enters is the characteristic decay time of that function. Since $\frac{d}{dt}(\dot{S}_q(t), \dot{S}_{-q}(0)) = 0$ at $t = 0$ we choose the simple parameterization

$$(\dot{S}^z_q(t),\ \dot{S}^z_{-q}(0))/(\dot{S}^z_q(0),\ \dot{S}^z_{-q}(0)) \approx \exp\left(-t^2/\tau_q^2\right), \tag{20}$$

giving Γ_q in terms of the parameter τ_q as

$$\Gamma_q = \frac{1}{2}\pi^{1/2}\ \tau_q\, (\dot{S}^z_q(0),\ \dot{S}^z_{-q}(0))/(S^z_q(0),\ S^z_{-q}(0)). \tag{21}$$

As before, the results are not highly sensitive to the Gaussian form of Eq. (20), which effectively implies a Gaussian cutoff to the Lorentzian Fourier transform of $f_q(t)$, at frequencies $\omega \sim \tau_q^{-1}$.

By using the identity

$$([H,\ A],\ B) = \langle [B,\ A] \rangle, \tag{22}$$

we can express $(\dot{S}^z_q, \dot{S}^z_{-q})$ in terms of $(S^z_q, S^z_{-q}) = \chi(q)$. This leads to the form

$$\Gamma_q = [\pi^{1/2}\, \tau_q\, k_B\, T\hbar^{-2}/\chi(q)]\ N^{-1} \sum_k [J(k) - J(k+q)]\, \chi(k). \tag{23}$$

With the Gaussian assumption (Eq. (20)) one can evaluate τ_q in terms of the second and fourth moments of the torque relaxation function. The necessary numerical calculations have been carried out by Reiter[22] for the simple cubic lattice. He finds that $\tau_q \approx h/JS$ is nearly independent of both q and T (maximum deviations of about ± 10% from a constant value) for the antiferromagnet, but that there is substantially greater variation in the ferromagnet, particularly below a temperature of $2T_c$. We will follow Moriya in taking τ_q = constant. Although this would appear to be a rather poor approximation for the ferromagnet, we show in the final section that for that case one nevertheless obtains results in quite good agreement with a more sophisticated theory due to Hubbard[23]. First, however, we consider corrections due to short range order to the MFA for $\chi(q)$, the other major approximation of the theory.

3. Short Range Order. The Onsager Correction to $\chi(q)$

The MFA gives an increasingly inappropriate estimate of $\chi(q)$ as the temperature approaches T_c, where the short range order of the ionic spins plays an important role. As Maarschall has pointed out[15], one can include these effects approximately in the study of NMR linewidths within a modified mean field theory which takes into account the Onsager Reaction Field[12]. The central idea is that the part of the local field acting on a given spin, which arises from the surrounding polarization due to the instantaneous orientation of the spin in question, should not be included in the effective orienting field. That polarization simply follows the motion of the spin in question and thus does not favor one orientation over another. This is a short range order effect which the MFA does not take into account.

In fact, as is well known, the MFA is not self-consistent, in that for exchange coupled spins at sites 1 and j it replaces $\langle \mathbf{S}_l . \mathbf{S}_j \rangle$ by $\mathbf{S}_l . \langle \mathbf{S}_j \rangle = 0$ for $T > T_c$, whereas the same correlation function as obtained directly from the MFA susceptibility

$$\langle \mathbf{S}_l . \mathbf{S}_j \rangle \sim \sum \chi(q) \exp\, [iq.(l-j)],$$

does *not* vanish. As Brout and Thomas have pointed out[13], a suitable choice of (temperature dependent) Onsager reaction field $\lambda(T)$ restores the self-consistency. Thus, subtracting $\lambda(T)$ from the simple molecular field $J(q)$, we find for the susceptibility

$$\chi(q) = \frac{\chi_0}{1-\chi_0[J(q)-\lambda(T)]} \tag{24}$$

and we require, by the definition of $\chi(q)$ in terms of the relaxation function (i.e., by the fluctuation-dissipation theorem),

$$\begin{aligned} N^{-1} \sum \chi(q) &= N^{-1} \sum (S^z_q(0),\ S^z_{-q}(0)) = \int_0^\beta d\lambda\, \langle S^z_j(-i\lambda)\, S_j(0) \rangle, \\ N^{-1} \sum J(q)\, \chi(q) &= \sum_j J_{jo}\, (S^z_j(0),\ S^z_o(0)), \end{aligned} \tag{25}$$

where j is again a site index. In a mean field theory, S^z_j commutes with the effective Hamiltonian, and $S^z(-i\lambda)$ can be replaced by S^z, so that $(S^z_j, S^z_l) \approx \approx \beta \langle S^z_j\ S^z_l \rangle$, Ref. 24. Then, Eq. (25) can be written as

$$N^{-1} \sum \chi(q) = \beta \langle (S^z_l)^2 \rangle = \beta\, S(S+1)/3 = \chi_o,$$

$$N^{-1} \sum J(q)\, \chi(q) = \beta \sum_j J_{jo} \langle S_j^z(0)\ S_o^z(0)\rangle. \tag{26}$$

From the definition (24), we have that

$$N^{-1} \sum [\chi_o^{-1} + \lambda(T) - J(q)]\, \chi(q) = 1$$

which, combined with Eq. (26), gives the requirement

$$\lambda(T) = \chi_o^{-1}\, \beta \sum_j J_{jo} \langle S_j^z(0)\ S_o^z(0)\rangle = \sum_j J_{jo} \frac{3\langle S_j^z(0)\ S_o^z(0)\rangle}{S(S+1)} \tag{27}$$

and we see that $\lambda(T)$ takes the form implied by the physical considerations discussed in the first paragraph of this section.

The Onsager correction, as one would expect, leads to an improved prediction of the magnetic critical temperature, T_c. Defining T_c as the highest temperature at which $\chi(q)$ diverges for some wave vector q, we have immediately from Eq. (24)

$$\chi_o^{-1}(T_c) = J(K_o) - \lambda(T_c), \tag{28}$$

where K_o identifies the wave vector for which the instability, and resulting magnetic ordering below T_c, occurs. In particular, $K_0 = 0$ for the ferromagnet. In the MFA, where $\lambda \equiv 0$, we find the simple result

$$k_B T_c^o = J(K_o)\, S(S+1)/3 \tag{29}$$

and we will sometimes find it convenient to express our results in terms of this quantity. Thus we write

$$\frac{\chi(q)}{\chi_o} = \frac{T/T_c^o}{s - J(q)/J(K_o)} \tag{30}$$

where $s = [1 + \chi_o \lambda(T)]T/T_c^o$ Now the self-consistency requirement (26),

$$(T/T_c^o) \int d^3q\, (2\pi)^{-3}\, [s - J(q)/J(K_o)]^{-1} = 1, \tag{31}$$

implicitly relates s and the temperature T. In particular, $s(T_c) = 1$, and $s(T) > 1$ for $T > T_c$. Furthermore, the integral

$$G(s) \equiv (2\pi)^{-3} \int d^3q\, [s - J(q)/J(K_o)]^{-1} \tag{32}$$

has been numerically tabulated[25] for the simple cubic, bcc, and fcc lattices.

The relation (31) between s and T,

$$G(s) = T_c^0/T, \qquad (33)$$

is readily solved numerically for these lattices. Then the susceptibility $\chi(q)$ is given immediately by Eq. (30). It will be shown below that this approach substantially improves the agreement between theory and experiment for the F^{19} NMR linewidth in MnF_2 and $KMnF_3$, as compared with the MFA.

The relaxation rate Γ_k is related by Eq. (23) to $\chi(q)$, given in our approximation by Eq. (30). We can write Γ_k in a particularly simple form in the common case where each spin is appreciably exchange coupled only to a single set of crystallographically equivalent spins (e.g., only to its nearest neighbors). Then it is readily shown that the sum in Eq. (23) can be written

$$\begin{aligned} N^{-1} \sum_k [J(k) - J(k+q)]\, \chi(k) &= N^{-1} [1 - J(q)/J(0)] \sum_k J(k)\, \chi(k) \\ &= [1 - J(q)/J(0)]\, \chi_o\, \lambda(T), \qquad (34) \end{aligned}$$

where the last equality follows directly from Eqs. (26) and (27). Then we have

$$\Gamma_q = \pi^{1/2}\, \tau_q \hbar^{-2}\, \frac{S(S+1)}{3} \left[1 - \frac{J(q)}{J(0)}\right] \frac{\lambda(t)}{\chi(q)} \,. \qquad (35)$$

In this form our result is readily compared with the expression used by Maarschall and others: $\Gamma_q \approx \text{const.}/\chi(q)$. The latter has been particularly useful[26] in the discussion of critical phenomena. If $\lambda(T)$ is slowly varying for $T \approx T_c$ (a reasonable expectation; short range order varies continuously through the critical point) and if the critical behavior is dominated by a small range of q near $K_0 \neq 0$, then this form and Eq. (35) will give very similar results. But Eq. (35) also correctly includes the long wavelength behavior: $\Gamma_0 = 0$ since $S^z(q=0)$ is a conserved quantity. This may be of relatively small importance in three dimensions, where the phase space at small q, a factor q^2dq in integrals, removes the divergence of $1/\Gamma_q$ which enters the expression for the linewidth; for example, see Eq. (41). In less than three dimensions, however, the small q behavior can play a dominant role in resonance behavior[27], and the approximation $\Gamma_q \approx \text{const.}/\chi(q)$ may no longer be useful, even in the critical region. Of course, Eq. (35) is also unsatisfactory in this case and must be suitably modified to remove the $q = 0$ divergences in physical integrals above $T = T_c$. Even in three dimensions the k-dependent factor $[1 - J(q)/J(0)]$ in Eq. (35) is of importance outside the critical region. The final factor $\lambda(T)$ in Eq. (35) also includes temperature dependence not found in the simpler approximation, which may be important if one is considering a wide range of temperatures above T_c.

Finally, for explicit calculations we can rewrite Eq. (35) once more, substituting for $\chi(q)$ and $\lambda(T)$ (see Eq. (30) and following line) their values as functions of s:

$$\Gamma_q = \pi^{1/2}\, \tau_q \hbar^{-2}\, J(K_o)\, k_B\, T \left[s - \frac{J(q)}{J(K_o)} \right] \left[1 - \frac{J(q)}{J(0)} \right] \left[\frac{sT_c^o}{T} - 1 \right] \cdot \tag{36}$$

4. The NMR Linewidth

The interaction between the nucleus and the electronic spins is generally characterized by a symmetric tensor F_j; see Eq. (1). We can choose as a coordinate system the principal axes of this tensor, such that

$$F_j^{\mu\nu} = \delta_{\mu\nu}\, A_j^{\mu\mu}. \tag{37}$$

In what follows we assume that all tensors F_j have the same principal axes and that the applied field H, is parallel to one of them. Of course, the more general case of non-collinear fields and principal axes may be easily obtained by convenient transformations of the coordinates.

From Eq. (6), the linewidth A $= 1/T_2 \sim \lim_{t\to\infty} [\Psi(t)/t]$, which is given explicitly by Eq. (4). We take the form (37) for F_j, make use of the symmetry

$$\langle\{S_j^x(t)\; S_{j'}^y(0)\}\rangle = \langle\{S_j^y(t)\; S_{j'}^x(0)\}\rangle \tag{38}$$

and recognize that $\langle\{S_j^\nu(t)\; S_{j'}^\nu(0)\}\rangle$ is independent of $\nu = x, y, z$, to obtain

$$\Delta = N^{-1}\, \hbar^{-2} \int_0^\infty d\tau \sum_q \left[|A^z(q)|^2 + \frac{1}{2}\, e^{i\omega_0\tau} \left(|A^x(q)|^2 + |A^y(q)|^2 \right) \right] \cdot \langle\{S_q^z(t)\; S_{-q}^z(0)\}\rangle, \tag{39}$$

where

$$A^\mu(q) = \sum_j A_j^{\mu\mu}\, e^{iq\cdot R_j}. \tag{40}$$

When we substitute for the correlation function, in Eq. (39), its value as given by Eqs. (11) and (18) and perform the integral over τ, neglecting the small nuclear resonance frequency ω_0 as compared to Γ_q. there is finally obtained for the linewidth

$$\Delta = k_B T \hbar^{-2} N^{-1} \sum_q \frac{|A(q)|^2 \chi(q)}{\Gamma_q}, \tag{41}$$

where

$$|A(q)|^2 = |A^z(q)|^2 + \frac{1}{2} [|A^x(q)|^2 + |A^y(q)|^2] \tag{42}$$

and $\chi(q)$ and Γ_q are given by Eqs. (30) and (36), respectively.

In Appendix A, we consider the asymptotic behavior of the linewidth at high temperatures and make comparison with more familiar forms for **A** in the $T = \infty$ limit.

5. The F^{19} Linewidth in MnF_2 and $KMnF_3$

A. Theory

In this Section, we use the theory presented above to obtain the temperature dependencies of the F^{19} NMR linewidth in MnF_2 and $KMnF_3$, and compare them with the experimental results.

$KMnF_3$ has the Perovskite structure with the Mn spins forming a s.c. lattice in the paramagnetic phase with near neighbor exchange, whereas MnF_2 has the Rutile (TiO_2) structure with Mn spins on a body centered tetragonal lattice. The primary exchange interaction in MnF_2 is between next-near-neighbors. The crystal structures and F^{19} local environments are shown in Fig. 1. For MnF_2, there are three neighboring Mn spins to each F. Mn(I) and Mn(I′), which belong to the same magnetic sublattice in the ordered state, are coupled by the same transferred hyperfine interaction tensor $\overleftrightarrow{A}$, to a given F nucleus, while Mn(II) belongs to the other sublattice and has a different hyperfine interaction with the same nucleus – i.e., $\overleftrightarrow{A}_{II} \neq \overleftrightarrow{A}_I$. In $KMnF_3$, there is an identical hyperfine coupling $\overleftrightarrow{A}$ of a F nucleus to the two symmetric Mn spins. The exchange couplings are also indicated in the figure. For MnF_2, $|J'| \ll |J|$. The hyperfine constants for both MnF_2 and $KMnF_3$ are given in Table I. In $KMnF_3$, the hyperfine tensor is diagonal with principal axes coinciding with the

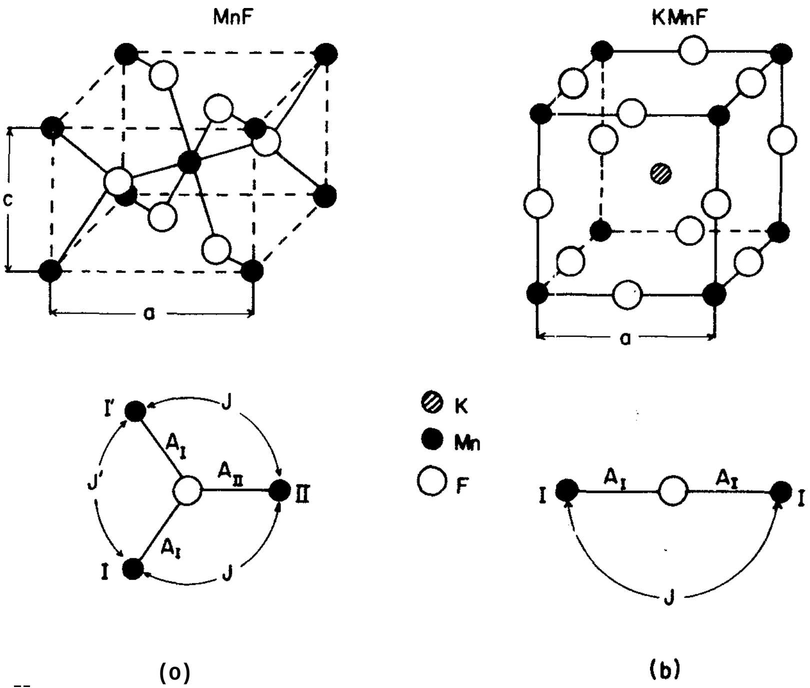

Fig. 1 — Unit cells for rutile (a) and cubic perovskite (b) structures. The local environment of a F^{19} nucleus is shown below with hyperfine and exchange interactions indicated explicitly.

cubic lattice vectors. In MnF_2, the off-diagonal element A, is small and will be neglected since it enters only to the second power in all calculations.

		A^{xx}	A^{yy}	A^{zz}	A^{yz}
MnF_2^a	Site I^c	11.81	15.57	17.83	4.4
	Site II	13.44	23.34	12.9	
$KMnF_3^b$		16.09	16.09	16.60	———

Table I — Values of the transferred hyperfine interaction constants in MnF_2 and $KMnF_3$. Units are 10^{-4} cm^{-1}.

(a) A. M. Clogston, J. P. Gordon, V. Jaccarino, M. Peter and L. R. Walker, Phys. Rev. 117, 1222 (1960).

(b) R. G. Shulmann and K. Knox, Phys. Rev. 119, 94 (1960).

c) The definitions of the cartesian axes in ref. a) are such that there is a $\pi/2$ rotation about the z axis when changing from Mn(I) to Mn(II).

Substituting the values R_j for the positions of the Mn ions into Eq. (40), we obtain for $KMnF_3$

$$|A^{\mu}(k)|^2 = 2(A^{\mu\mu})^2 \; (1 + \cos k_x a), \tag{43a}$$

and for MnF_2

$$\begin{aligned} |A^{\mu}(k)|^2 = 2(A_I^{\mu\mu})^2 &+ (A_{II}^{\mu\mu})^2 + 2(A_I^{\mu\mu})^2 \cos 2\,!\cdot \\ &+ 4\,\text{A?'' A?? cos (c + \textasciitilde)cos}\; \zeta_{/} \end{aligned} \tag{43b}$$

where

$$\xi = \frac{1}{2}\, ak_x, \quad \eta = \frac{1}{2}\, ak_y, \quad \zeta = \frac{1}{2}\, ck_z$$

and a, c are lattice constants.

Substituting the hyperfine constants from Table I into Eqs. (42) and (43), we find in units of $10^{-8}\,\mathrm{cm}^{-2}$, for $KMnF_3$

$$|A(k)|^2 = 534\,(1 + \cos k_x a) \tag{44a}$$

and

$$|A(k)|^2 = 500\,[3.09 + 2.04 \cos 2\zeta + 3.93 \cos(\xi+\eta) \cos \zeta], \tag{44b}$$

for MnF_2. It is interesting to note that Eq. (44b) is nearly the same result that would be obtained if $A_I^{\mu} = A_{II}^{\mu\mu}$, i.e.

$$|A(k)|^2 = \text{const.}\; [3 + 2 \cos 2\zeta + 4 \cos(\xi + \eta) \cos \zeta].$$

This result is coincidental.

For the final evaluation of Eq. (41), it is necessary to know the function $J(k)/J(0)$.

The substitution of the lattice positions of the magnetic ions into Eq. (15) leads to the results

$$\frac{J(\mathbf{k})}{J(0)} = \frac{1}{3}\,(\cos k_x a + \cos k_y a + \cos k_z a) \tag{45a}$$

for $KMnF_3$, and

$$\frac{J(\mathbf{k})}{J(0)} = \left[\frac{4J}{4J+J'}\right] \cos \xi \cos \eta \cos \zeta + \left[\frac{J'}{4J+J'}\right] \cos 2\zeta \tag{45b}$$

for MnF_2. The first term on the right hand side of (45b) is the dominant one and we shall henceforth neglect J' altogether. We note that we can then continue to use Eq. (34) for MnF_2 as well as for $KMnF_3$. In each case $J(K_o) = -J(0)$.

The evaluation of the linewidth for the simple cubic case is straighforward once Eq. (41) is expressed in terms of the tabulated integrals in Eq. (32) and their derivatives. First, as usual, the sum over k in Eq. (41) is replaced by a triple integral over k-space. After substituting from Eqs. (30), (36), (44a) and (41), we find an expression of the form given by Hess and Hunt[28] for $KMnF_3$:

$$\frac{\Delta}{\Delta_\infty} = \frac{2[G(1) + G(s)]\,(1+s)^{-2} + (s-1)\,(\partial G(s)/\partial s)\,(1+s)^{-1}}{6[sG(s) - 1]\;[2G(0) - 1]}. \tag{46}$$

We compute the linewidth only relative to its value at infinite temperature.

The evaluation of Eq. (41) for the MnF_2 structure is somewhat more complex. Using the value of $\chi(q)$ given in Eq. (30) and obtaining for each temperature the corresponding value of s via the prescription given by Eq. (33), we obtain an integral of the form

$$\int_{-\pi}^{+\pi} \frac{d\xi\, d\eta\, d\zeta}{(2\pi)^3}\, \frac{[c_1 + c_2 \cos 2\zeta + c_3 \cos(\xi + \eta)\cos\zeta]}{(s+\gamma)^2\,(1+\gamma)} \tag{47}$$

where c_1, c_2, and c_3 are the coefficients in Eq. (44b) and $\gamma = -\cos\xi\,\cos\eta\,\cos\zeta$. The details of the evaluation of this integral are given in Appendix B. It is important to note that the Onsager correction appears in these calculations only in the functional dependence of the variable s on temperature. Also, this is the only way in which temperature appears. Thus, insofar as linewidth calculations are concerned, the Onsager correction is equivalent to a nonlinear rescaling of the temperature, the correction being most significant in the immediate vicinity of T_c^o.

B. Experiment

Experiments were carried out on conventional crossed-coil c.w. NMR spectrometers operating at 15.6 mHz and 60 mHz. No frequency dependence to the NMR linewidths was observed. Single crystal samples were shaped to approximate ellipsoids of revolution to minimize demagnetizing field corrections. Temperature was regulated to within 1°K using a heated stream of cold N_2 gas. Linewidths reported are the separation in field units between the extrema of a derivative resonance signal. All resonances have the Lorentzian shape, characteristic of exchange-narrowed hyperfine broadened profiles[10].

Due to the anisotropy of the hyperfine interaction in both $KMnF_3$ and MnF_2, there are magnetically inequivalent fluorine sites for arbitrary crystal orientations relative to the external field. For the data given here the samples were oriented as follows: MnF_2 was positioned such that the external field H_0 was parallel to the crystal c axis (see Fig. 1) where all sites are equivalent and a single resonance line is observed; $KMnF_3$ was positioned with H, along a cubic axis and two separately resolved resonances result. The resonance studied was the one for which H_0 is directed perpendicular to the Mn-F bond direction. Actual data was taken up to 600K. An experimental value of $\Delta_{T=\infty}$ was then obtained by plotting $\Delta(T)$ vs $1/T$ and extrapolating to $T = \infty$ as has been done in high temperature expansions of the linewidth[29]. In this manner we obtain $\Delta H_{pp}(\infty)_{KMnF_3} =$ $= 22.6$ Oe, and $\Delta H_{pp}(\infty)_{MnF_2} = 44.6$ Oe.

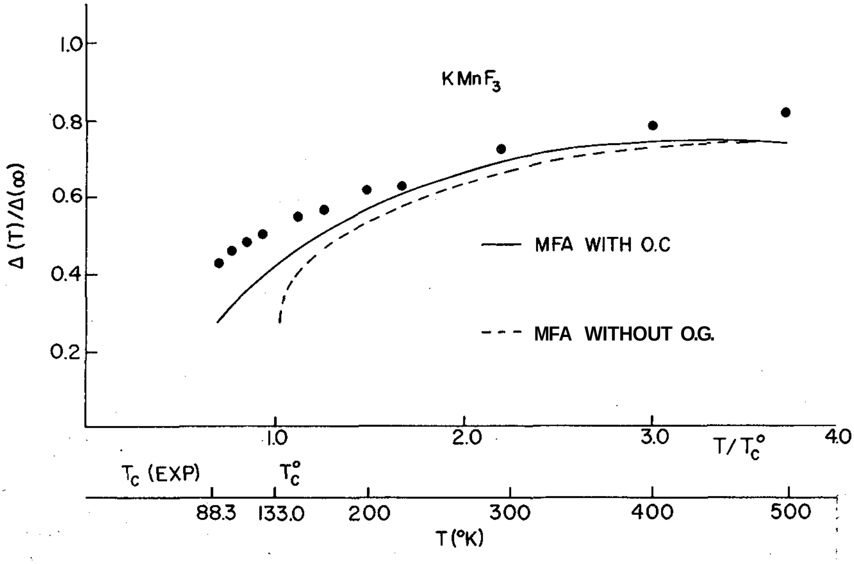

Fig. 2 — Temperature dependence of F^{19} NMR linewidth in $KMnF_3$ relative to "infinite temperature" value (see text). Calculated linewidth ratios from the Moriya theory with (solid line) and without (dashed line) Onsager corrections are shown.

In Figures 2 and 3, we compare experimental linewidths with calculations from Eqs. (50) and (51). The linewidth in the cubic case does not diverge at the Néel temperature. The critical fluctuations at q $= K_0$ correspond to antiparallel alignment of the two neighboring Mn spins to a given F nucleus, so the amplitude of the corresponding hyperfine field vanishes by symmetry[15]. It is apparent that the Moriya theory, with or without Onsager corrections, yields semi-quantitative agreement with experiment for the two systems studied. However, for both MnF_2 and $KMnF_3$, the Onsager corrections provide improved agreement with experiment, particularly in the vicinity of the ordering temperature. The lack of agreement, in scale, at high temperature, may be attributed either to the extrapolation procedure for obtaining $(\Delta H)_\infty$ or to the fact that the hyperfine interaction is noticeably temperature dependent above 300 – 600 K, necessitating appropriate corrections to be made to ΔH_∞. This is currently being investigated in our laboratory.

	J	J'	T_c^o	T_c(O.C.)	T_c(Exp)
MnF_2	-1.76^a	$+0.32^a$	85.9	61.7	67.3^c
$KMnF_3$	-3.8^b	0	133.0	87.8	88.3^d

Table II. Computed values for the antiferromagnetic transition temperature are shown for the uncorrected MFA (T_c^o) and with Onsager corrections (T_c(O.C.)). Calculations are based upon the exchange constants (J, J') given. Experimentally determined values of T_c are shown for comparison. All quantities given in degrees Kelvin.

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Short range order effects substantially modify the predicted values of the critical temperatures. The values for T_c with Onsager corrections (O.C.), obtained from Eq. (33) are T_c(O.C.) $= 0.66\ T_c^o$ for simple cubic systems (e.g., $KMnF_3$) and T_c(O.C.) $= 0.72\ T_c^o$ for the body centered structures (e.g., MnF_2). The former value is in good agreement with a Green's function calculation in the random phase approximation made by Lines[30]. T_c^o is computed from known values of the exchange constants (given in Table II) and Eq. (29). In computing T_c^o for MnF_2, a correction due to the small near-neighbor ferromagnetic exchange coupling is taken into account. The various theoretical transition temperatures are compared with experimental ones in Table II. It is seen that the T_c(O.C.) agrees well with T_c(Exp.),

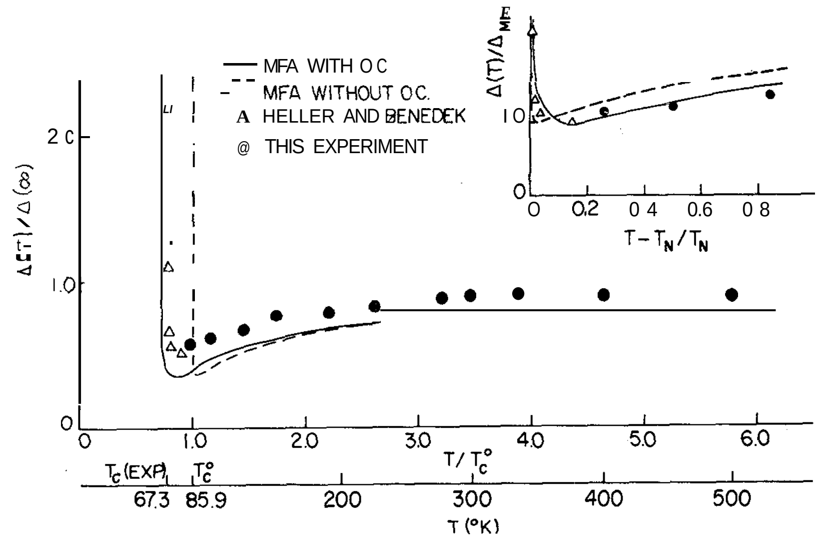

Fig. 3 — Temperature dependence of F^{19} NMR linewidth in MnF_2. Moriya theory linewidths with (solid line) and without (dashed line) Onsager corrections are shown. The inset shows details of the minimum linewidth region where normalization made to the minimum linewidth rather than to the "infinite temperature" linewidth.

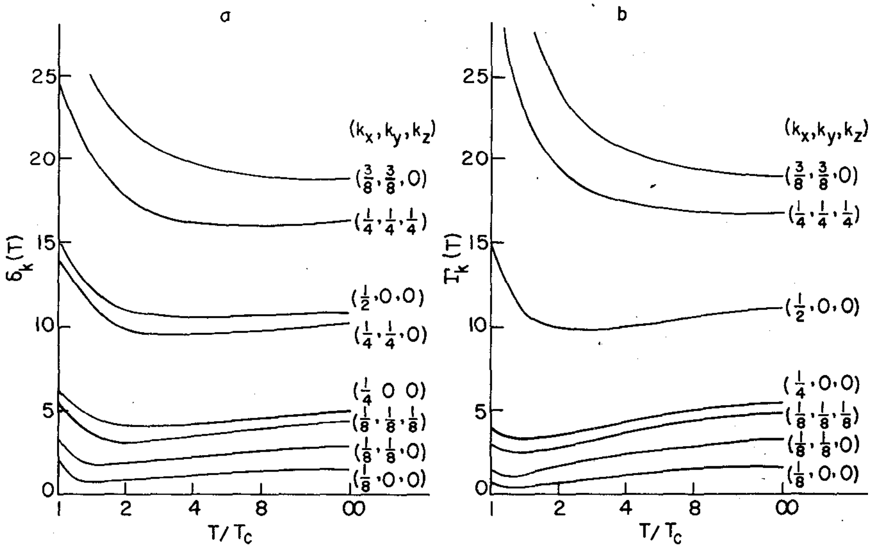

Fig. 4 — Comparison is made between the temperature and wave-vector dependence of Γ_k the spin correlation function decay constant of the present theory and the closely related quantity δ_k that appears in Hubbard's numerical calculations[23]. All results here are for the simple cubic *ferromagnet* with nearest neighbor exchange interactions. Details are given in the text.

particularly for the cubic system. Apparently there is a tendency for the O.C. theory to slightly underestimate T_c, whereas the uncorrected MFA seriously overestimates T_c.

6. Comparison with Hubbard's Correlation Function Theory

It is possible to make limited comparison between our analytical results and other more recent theoretical work on the dynamical behavior of the spincorrelation function of the Heisenberg systems in the paramagnetic phase[22, 23, 31, 32]. Since these latter results for the correlation function involve non-linear integro-differential equations, they are somewhat difficult to compare directly with our theory. However, we can immediately compare our numerical results for Γ_k with the corresponding quantities calculated by Hubbard[23] for the simple cubic ferromagnet.

Hubbard's results are given in terms of the quantity

$$\hat{F}_k(\omega) = 2 \int_0^{\infty} f_k(t) \cos \omega t \, dt. \tag{48}$$

Using Eq. (18), we obtain

$$\hat{F}_k(0) = \frac{2}{\Gamma_k} \cdot \tag{49}$$

Hubbard points out that the shapes of the curves $\hat{F}_k(\omega)$ are such that, to a reasonably good approximation,

$$\hat{F}_k(0) \sim \frac{\pi}{\delta_k}, \tag{50}$$

where δ_k is the half-width of $F_k(\omega)$ at half height. In the discussion following Eq. (18), in fact, we have interpreted Γ_k in this somewhat generalized sense, recognizing that the exponential form is not valid for all k at all temperatures. From Eqs. (49) and (50), it follows that

$$\Gamma_k \propto \delta_k . \tag{51}$$

In Fig. 4a, we have re-drawn Hubbard's calculated values of δ_k for the case of a simple cubic ferromagnet. The spherical model temperature scale is used because, as is shown by Brout and Thomas[13], it is equivalent to the Onsager Corrected MFA to second order in the reaction field. Fig. 4b represents Γ_k as given by Eq. (36) with τ_k taken to be constant. The quantity

Γ_k is normalized in such a way that

$$\Gamma_k\ [\mathbf{k} = (1/2,\ 0,\ 0);\ \ T = \infty] = \delta_k.$$

The components of k are written in units of $2\pi/a$, where a is the lattice constant. The reasonably good agreement between Figs. 4a and 4b provide a heuristic justification for the approximation of taking τ_k to be a constant. Unfortunately, a numerical calculation of Hubbard's theory for the antiferromagnet is not available. We might expect, however, that reasonably good agreement between his results and our Γ_k would result in that case as well. We have pointed out above that calculations by Reiter[22] suggest that the replacement of τ_k by a constant is a better approximation in that case than it is for the ferromagnet.

Appendix A

It is of some interest to examine the high temperature behavior of certain of the formulae given in the text, with the view in mind of obtaining an estimate for the torque correlation decay time in this limit. For example, as T ⟶ ∞, $\chi(q) \longrightarrow \chi_0 = S(S+1)/3k_BT$ and Eq. (41) becomes

$$\Delta_\infty = \frac{1}{3}\, S(S+1)\, \hbar^{-2}\, N^{-1} \sum_q \frac{|A(q)|^2}{\Gamma_q}. \tag{A-1}$$

For the important case of a nucleus of an ion interacting only with the spin moment of the same ion (e.g., Mn^{55} in MnF_2) then $|A(q)|^2 = A^2$, independent of q, and **(A-1)** reduces to

$$\Delta_\infty = A^2\, \hbar^{-2}\, \frac{1}{3}\, S(S+1)\, N^{-1} \sum_q \Gamma_q^{-1}. \tag{A-2}$$

In this T ⟶ ∞ limit, the low order moments of the line profile $I(\omega)$ have been calculated exactly. With any reasonable assumption (e.g., a suitably truncated Lorentzian) on the form of $I(\omega)$, these results imply[10]

$$\Delta_\infty = C\, A^2 \hbar^{-2} \frac{1}{3}\, S(S+1)\, \omega_e^{-1}, \tag{A-3}$$

where $\omega_e^2 = 2z(J/\hbar)^2\, S(S+1)/3$ is the square of the "exchange frequency" and C is a constant of order unity whose precise value depends on the details of the assumed form of $I(\omega)$. Then we can make the identification

$$N^{-1} \sum_4 \Gamma_q^{-1} = \omega_e \qquad (T \longrightarrow \infty). \tag{A-4}$$

The T ⟶ ∞ limit of Γ_q – or even the fact that the finite limit exists, as implied by (A-4) – is not immediately transparent in the form (36) for Γ_q. High temperature expansion of Eqs. (32)

and (33), for a lattice with nearest neighbor antiferromagnetic exchange, gives

$$s \approx (T/T_c^0)\,[1 + z^{-1}\,(T_c^0/T)^2], \tag{A-5}$$

where z is the number of nearest neighbors. The second term in brackets is the lowest order correction to MFA due to short range order. It is clearly essential to keep this correction for the last factor of Eq. (36) even in the $T \longrightarrow \infty$ limit. Then

$$\Gamma_q \approx \frac{1}{2}\,\pi^{1/2}\,\tau\,\omega_e^2\,[1 - J(q)/J(0)], \qquad (T \longrightarrow \infty) \tag{A-6}$$

Since

$$N^{-1} \sum_q\, [1 - J(q)/J(0)]^{-1} \equiv G(1) \tag{A-7}$$

is a number of order unity, we have from (A-4) and (A-6) that $\tau\omega_e \sim 1$. This is consistent with the view that the torque correlation functions decay in a time τ of the order of the microscopic exchange time ω_e^{-1}, rather than a longer time associated with some collective motion.

Appendix B

The integral Eq. (47) can be decomposed by partial fractions into integrals of the form:

$$I_1 = \int \frac{d\xi\, d\eta\, d\zeta}{(2\pi)^3}\,\frac{1}{s+\gamma}, \qquad I_2 = \int \frac{d\xi\, d\eta\, d\zeta}{(2\pi)^3}\,\frac{1}{(s+\gamma)^2}$$

$$I_3 = \int \frac{d\xi\, d\eta\, d\zeta}{(2\pi)^3}\,\frac{\cos^2\zeta}{s+\gamma}, \qquad I_4 = \int \frac{d\xi\, d\eta\, d\zeta}{(2\pi)^3}\,\frac{\cos^2\zeta}{(s+\gamma)^2}.$$

Integral I_1 is just $G(s)$ (see Eq. (32)) and integral I_2 is its derivative $G'(s)$. Tabulated values for $G(s)$ are available[25]. Integral I_3 can be transformed into one which is more convenient for numerical integration by using the symmetry properties of the integrand and performing the integral over ζ analytically. The result is

$$I_3 = I_1 - \frac{2}{\pi^2}\int_0^{\pi/2} \frac{d\xi\, d\eta}{s + (s^2 - \cos^2\xi\cos^2\eta)^{1/2}}.$$

Similarly, one gets

$$I_4 = I_2 - \frac{2s}{\pi^2}\int_0^{\pi/2} \frac{\sin^2\zeta\, d\eta\, d\zeta}{(s^2 - \cos^2\eta\cos^2\zeta)^{3/2}}.$$

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