Nuclear Resonance Studies of Magnetic Critical Fluctuations in MnF_2*

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Atomic nuclei with magnetic moments can serve to probe the local fields within magnetic materials. By studying the nuclear resonance frequency and line width in the critical temperature region near the magnetic transition, it is possible to obtain precise and detailed information [1, 2] on the establishment of magnetic order. Here we shall be concerned with the effect of the critical fluctuations on the NMR line width: associated with the approach to the critical temperature T_c the nuclear resonance lines in ferro- and antiferromagnets exhibit a remarkably rapid broadening. A very detailed study of this effect has been made for the case of the antiferromagnet MnF_2. ($T_c = 67.336$ °K, also denoted by T_N). These experiments shed light on the behavior of the electron spin correlation functions in the critical region. In this account we show that the experimental data implies a "slowing down" of the spin fluctuations in the critical region. A simple physical model for the time dependence of the correlation functions will then be presented. This model yields a theory which is in satisfactory accord with the observed broadening of the F^{19} resonance in MnF_2 as T approaches T_c from above.

The line width anomaly at the critical point for the F^{19} resonance in MnF_2 is shown in figure 1. We shall be largely concerned with the situation in the paramagnetic state $T > T_c$. The detailed behavior of the line width in the region $T_c + 0.006$ °K $< T < T_c + 10$ °K is shown by the experimental points in figure 2. (The drawn lines correspond to the theory to be outlined below.) The line-width is anisotropic with respect to the direction of the externally applied d-c field $\mathbf{H}_0$. For $\mathbf{H}_0$ along c (the antiferromagnetic axis), the line broadens by about a factor of ten as T_c is approached. In the region of severe broadening, the ratio of the line width for $\mathbf{H}_0$ along the c-axis to the line width for $\mathbf{H}_0$ along the a-axis is very nearly 2 to 1,

$$\delta\nu_c/\delta\nu_a = 2. \qquad (1)$$

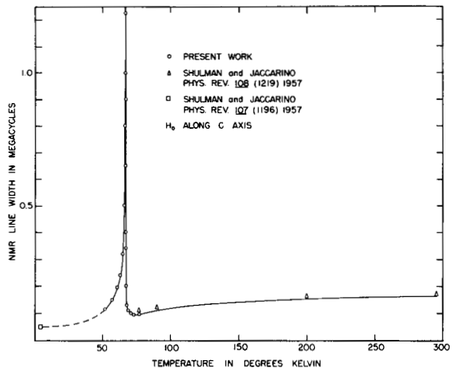
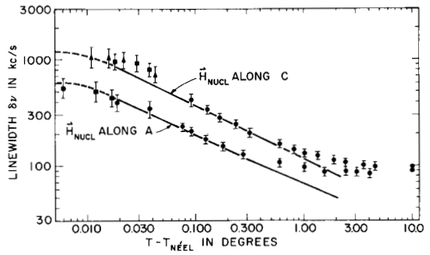


FIGURE 1. *Temperature dependence of* F^{19} *nuclear resonance line width in* MnF_2 *from 4 °K to 300 °K.*
Applied field along c-axis.



COMPARISON OF THEORY WITH EXPERIMENT, $T > T_N$
$\lambda = 2.7 \times 10^{12}$ sec^{-1}

FIGURE 2. *Experimental* F^{19} *line widths in* MnF_2 *just above* T_c.
Drawn curves represent theoretical results with $\lambda = 2.7 \times 10^{12}$ sec^{-1}.

Just above T_c, the line widths level off at the values

$$\delta\nu_c(T_c) = 1100 \text{ kc/sec}$$

$$\delta\nu_a(T_c) = 550 \text{ kc/sec}. \qquad (2)$$

One observation, made at 200 mdeg above T_c, showed that the line width increases monotonically as $\mathbf{H}_0$ is turned from the a to the c direction. At 77 °K, where the line is relatively narrow, the line width is essentially isotropic.

We would like to understand these results. One possible mechanism for the line width broadening will now be stated and then shown to be incompatible with the experimental facts. Suppose that as T_c was neared, the electron spins in the sample became permanently ordered to a degree which varied from one region to another. This would result in a variation $\Delta\mathbf{H}$ in the time average local field seen by different nuclei. We assume the direction of antiferromagnetic spin alinement within each region to be along the c-axis, the direction of antiferromagnetic alinement below T_c. The direction of $\Delta\mathbf{H}$ will then also be along c. The nuclear resonance would then be inhomogeneously broadened. This broadening would be severe if the applied field $\mathbf{H}_0$ were colinear with $\Delta\mathbf{H}$. On the other hand, if $\mathbf{H}_0$ were perpendicular to $\Delta\mathbf{H}$, the observed broadening would be of the second order in $|\Delta H|$. A simple calculation shows that if this were the mechanism responsible for the line width, the anisotropy factor $\delta\nu_c/\delta\nu_a$ would be very much greater than 2, in contradiction with the experimental results.

The line width is therefore to be attributed to fluctuations in the local hyperfine fields seen by the nuclei; it can then be related to the electron spin correlation functions in a way that may be expressed quantitatively as follows. If the interaction between a nucleus and an electron spin has the form $\mathscr{H} = A\mathbf{I}\cdot\mathbf{S}$, where A is the hyperfine coupling constant, and if z is the direction of the average local field at the nucleus and furthermore if the correlation time for the spin fluctuations is short compared with the nuclear Larmor frequency, then [3, 4]

$$\delta\nu = \frac{1}{\pi\sqrt{3}}\left(\frac{A}{\hbar}\right)^2 \int_0^\infty dt \Big[< \{\delta S_z(t)\delta S_z(0)\} >$$

$$+ \frac{1}{2} < \{\delta S_x(t)\delta S_x(0)\} > + \frac{1}{2} < \{\delta S_y(t)\delta S_y(0)\} > \Big]. \qquad (3)$$

Here $\delta S(t) = S(t) - < S >$ denotes the departure of the spin from its thermal average value and $\{AB\} = \frac{1}{2}(AB + BA)$.

We now show that in order to explain the line width anomaly within the framework of the formula (3), it must be assumed that the time dependence of the spin correlation functions becomes "slow" near T_c. Let

$$G_\mu(t) = \frac{< \{\delta S_\mu(t)\delta S_\mu(0)\} >}{< [\delta S_\mu(0)]^2 >},$$

where $\mu = 1, 2, 3$ denotes a Cartesian component, and define correlation times τ_μ by writing

$$\tau_\mu = \int_0^\infty G_\mu(t)dt.$$

Then (3) becomes

$$\delta\nu = \frac{1}{\pi\sqrt{3}}\left(\frac{A}{\hbar}\right)^2 \Big[\tau_z < (\delta S_z)^2 >$$

$$+ \frac{1}{2}\tau_x < (\delta S_x)^2 > + \frac{1}{2}\tau_y < (\delta S_y)^2 > \Big]. \qquad (4)$$

The experimental line width was found to be isotropic above $T_c + 10$ °K. We then surmise that in this temperature range the spin fluctuations are isotropic and $\tau_x = \tau_y = \tau_z = \tau$. If the correlation times were constant as $T \to T_c$ we would have

$$\delta\nu = \frac{1}{\pi\sqrt{3}}\left(\frac{A}{\hbar}\right)^2 \tau \Big[< (\delta S_z)^2 >$$

$$+ \frac{1}{2} < (\delta S_x)^2 > + \frac{1}{2} < (\delta S_y)^2 > \Big].$$

But for $T > T_c$, $< S > = 0$, and the following identity holds

$$< (\delta S_x)^2 > + < (\delta S_y)^2 > + < (\delta S_z)^2 > = S(S+1) = \frac{5}{2}\frac{7}{2}.$$

From this it may be seen that the temperature dependence of the time independent correlations $< (\delta S_\mu)^2 >$ cannot be responsible for the tenfold increase in line width observed as $T \to T_c$. The correlation times evidently increase in the critical region.

The observed line width anisotropy is now interpreted as follows. Denoting the crystal axes by

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c, a, and a', the line widths for the average local field along c and a are given respectively by

$$\delta\nu_c=\frac{1}{\pi\sqrt{3}}\left(\frac{A}{\hbar}\right)^2\left[\tau_c<(\delta S_c)^2>+\frac{1}{2}\tau_a<(\delta S_a)^2>+\frac{1}{2}\tau_{a'}<(\delta S_{a'})^2>\right]$$

and

$$\delta\nu_a=\frac{1}{\pi\sqrt{3}}\left(\frac{A}{\hbar}\right)^2\left[\tau_a<(\delta S_a)^2>+\frac{1}{2}\tau_c<(\delta S_c)^2>+\frac{1}{2}\tau_{a'}<(\delta S_{a'})^2>\right].$$

Therefore, the factor of 2 anisotropy actually observed just above T_c implies that at those temperatures

$$\tau_c<(\delta S_c)^2>\gg\tau_a<(\delta S_a)^2>. \tag{5}$$

A theory of the electron spin correlation functions in the critical region was given by Moriya [5]. The physical content of the theory may be expressed in the following terms. Just above T_c there exists a short range antiferromagnetic correlation between the spins. Roughly speaking, the spin arrangement at any instant of time consists of clusters of antiferromagnetically alined spins. The time average value of the spin at any site is zero, however, and so these clusters are constantly forming, dissolving and reforming. The average size *and lifetime* of the clusters increases as $T\to T_c$. This latter point, which corresponds to a "slowing" of the spin fluctuations is an essential part of the theory. The direction of antiferromagnetic alinement within the clusters is mainly along the c-axis; this is responsible for the inequality (5) and the consequent line width anisotropy.

On the basis of this picture it is clear that we should rewrite eq (3) in terms of the Fourier transform spin deviations $\delta\mathbf{S}_k(t)$. These are defined in terms of the ionic spin deviations $\delta\mathbf{S}_j(t)$ as follows

$$\delta\mathbf{S}_j(t)=\frac{1}{\sqrt{N}}\sum_k\delta\mathbf{S}_k(t)e^{-ik\cdot r_j}. \tag{6}$$

The theory is greatly simplified if we assume that the correlation functions for the Fourier transformed spin deviations decay exponentially with time, i.e.,

$$<\{\delta S_{k\mu}(t)\delta S^+_{k\mu}(0)\}>=<|\delta S_{k\mu}(0)|^2>e^{-\Gamma_\mu(k)t}. \tag{7}$$

Using eq (7) and (6) in eq (3) it follows that

$$\delta\nu_c=\frac{1}{\pi\sqrt{3}}\left(\frac{A}{\hbar}\right)^2\frac{1}{N}\sum_k\left[\frac{<|\delta S_{kc}(0)|^2>}{\Gamma_c(k)}+\frac{1}{2}\frac{<|\delta S_{ka}(0)|^2>}{\Gamma_a(k)}+\frac{1}{2}\frac{<|\delta S_{ka'}(0)|^2>}{\Gamma_{a'}(k)}\right] \tag{8}$$

when the average local field is along the c-axis. If the average local field is along the a-axis one interchanges c and a.

The tenfold increase in the line width that is observed to occur as $T\to T_c$ from above can now be understood as follows. As $T\to T_c$, the quantities $<|\delta S_{kc}(0)|^2>$ become very large while the corresponding decay rates $\Gamma_c(k)$ become very small for wave vectors k near the antiferromagnetic made k_0. This corresponds to the physical picture of increased correlation range and cluster lifetime near T_c.

To make a quantitative theory of these effects we thus need to know the temperature dependence of both the quantities $<|\delta S_{k\mu}|^2>$ and $\Gamma_\mu(k)$. In his theory, Moriya used the fluctuation-dissipation theorem to relate $<|\delta S_{k\mu}|^2>$ to the wavelength dependent d-c susceptibilities. The relation is

$$<|\delta S_{k\mu}|^2>=\frac{k_BT}{g^2\mu_B^2}\chi_\mu(k), \tag{9}$$

where k_B is the Boltzman constant, μ_B the Bohr magneton, and $g=2$. The susceptibilities $\chi_\mu(k)$ can be calculated on a molecular field model. The results are given by Moriya [5].

To calculate the decay rates $\Gamma_\mu(k)$, Moriya employed a technique developed by Mori and Kawasaki [6] for describing spin diffusion in ferromagnets. Here, however, we shall employ a very simple physical model. According to this view [7], the decay of a staggered spin configuration is inhibited by the staggered molecular field generated by that configuration, an effect which leads to a particularly slow decay near T_c. On this model the decay rates are related to the wavelength dependent d-c susceptibilities as follows

$$\Gamma_\mu(k)=\lambda\frac{\chi_{\text{Curie}}(T)}{\chi_\mu(k,T)}, \tag{10}$$

where λ is a temperature independent parameter, and

$$\chi_{\text{Curie}}(T)=\frac{g^2\mu_B^2S(S+1)}{3k_BT} \tag{11}$$

is the Curie susceptibility.

The motivation behind eq (10) is as follows. Imagine that at some temperature $T>T_c$ we artificially produced a "staggered magnetization" M_s by applying a staggered field H_s. If H_s is turned off, M_s eventually relaxes to zero. Consider the situation at the instant that H_s is turned off. According to the viewpoint of the Weiss theory, where the coupling between the spins is replaced by an effective field, the spins would find themselves in a staggered "molecular field." We suppose this field to be strong enough to produce a staggered magnetization M_s^* at equilibrium. Evidently $M_s^*=f(T)M_s$ where $f(T)$ is a fraction which becomes equal to unity at T_c, that being the temperature at which the magnetization becomes self-sustaining. As a model to describe the decay of the staggered magnetization we now write the following differential equation

$$\frac{dM_s}{dt}=-\lambda(M_s-M_s^*)=-\lambda[1-f(T)]M_s.$$

This leads to an exponential decay $M_s=M_s(0)e^{-\Gamma_st}$ where

$$\Gamma_s=\lambda[1-f(T)]. \tag{12}$$

Now let us calculate the staggered magnetization M_s produced at equilibrium by a staggered field H_s. In the absence of the molecular field we would have $M_s=H_s\chi_{\text{Curie}}$ where χ_{Curie} is given by (11). In the presence of the molecular field

$$M_s=H_s\chi_{\text{Curie}}+f(T)M_s$$

or

$$M_s=\frac{H_s\chi_{\text{Curie}}}{1-f(T)}.$$

Thus the "staggered susceptibility" is effectively

$$\chi_s=\frac{\chi_{\text{Curie}}}{1-f(T)}. \tag{13}$$

Comparing (13) with (12) we find

$$\Gamma_s=\lambda\frac{\chi_{\text{Curie}}}{\chi_s}.$$

The same argument may be applied to relate the relaxation of spin arrangements of arbitrary wavelength to the corresponding susceptibilities. We thus obtain eq (10). In applying this relation to a calculation of the time dependence of the correlation functions, we are assuming that the time decay in the kth Fourier component of the magnetization which occurs as a result of spontaneous fluctuations is similar to that which characterizes the return to equilibrium following an artificially produced non-equilibrium state.

The line width may now be expressed in terms of the wavelength dependent susceptibilities and the parameter λ. Using (9), (10), and (11) in (8) we find

$$\delta\nu_c=\frac{1}{\lambda}\frac{1}{\pi\sqrt{3}}\frac{A^2}{\hbar^2}\left(\frac{k_BT}{g^2\mu_B^2}\right)^2\frac{3}{S(S+1)}\frac{1}{N}\sum_k[\chi_\parallel^2(k)+\chi_\perp^2(k)] \tag{14}$$

$$\delta\nu_a=\frac{1}{\lambda}\frac{1}{\pi\sqrt{3}}\frac{A^2}{\hbar^2}\left(\frac{k_BT}{g^2\mu_B^2}\right)^2\frac{3}{S(S+1)}\frac{1}{N}\sum_k\left[\frac{1}{2}\chi_\parallel^2(k)+\frac{3}{2}\chi_\perp^2(k)\right],$$

where $\chi_{||}(k)$ and $\chi_\perp(k)$ denote the components of the wavelength dependent susceptibilities respectively parallel and perpendicular to the c-axis.

The discussion so far has assumed that each fluorine nucleus is coupled to a single manganese spin. In actual fact, there are three spins to which the coupling is important [8]. We denote these by $\mathbf{S}$, $\mathbf{S}'$, and $\mathbf{S}''$, their positions in the lattice by r, r', and r'' and the corresponding hyperfine coupling tensors by $\mathbf{A}$, $\mathbf{A}'$ and $\mathbf{A}''$. We then replace the coupling $A\mathbf{I}\cdot\mathbf{S}$ in the preceding discussion by the coupling $\mathbf{I}\cdot(\mathbf{A}\cdot\mathbf{S}+\mathbf{A}'\cdot\mathbf{S}'+\mathbf{A}''\cdot\mathbf{S}'')$. The line width formulae (14) then become revised in a way which can be expressed compactly as follows. For each

wave-vector k construct the tensor

$$\mathbf{A}(k)=\mathbf{A}e^{ik\cdot r}+\mathbf{A}'e^{ik\cdot r'}+\mathbf{A}''e^{ik\cdot r''}. \tag{15}$$

For the present purposes, the principal axes can be taken to be along the $c=[100]$, $x=[110]$ and $y=[1\bar{1}0]$ directions. Then the line widths can be written

$$\delta\nu_c=\frac{1}{\lambda}\frac{\hbar^{-2}}{\pi\sqrt{3}}\left(\frac{k_BT}{g^2\mu_B^2}\right)\frac{3}{S(S+1)}\frac{1}{N}$$
$$\sum_k\left[|A_{cc}(k)|^2\chi_{\parallel}^2(k)+\frac{|A_{xx}(k)|^2+|A_{yy}(k)|^2}{2}\chi_{\perp}^2(k)\right] \tag{16}$$

$$\delta\nu_a=\frac{1}{\lambda}\frac{\hbar^{-2}}{\pi\sqrt{3}}\left(\frac{k_BT}{g^2\mu_B^2}\right)\frac{3}{S(S+1)}\frac{1}{N}\sum_k\left[\frac{1}{2}\right.$$
$$\left.|A_{cc}(k)|^2\chi_{\parallel}(k)+\frac{3}{2}\frac{|A_{xx}(k)|^2+|A_{yy}(k)|^2}{2}\chi_{\perp}^2(k)\right].$$

Since the modes $k\cong k_0$ make the most significant contribution near T_c, we can replace $\mathbf{A}(k)$ by $\mathbf{A}(k_0)$. The numerical values of the tensor components can be obtained from the electron spin resonance experiments [8] on Mn^{++} in ZnF_2 and may be expressed as follows

$$\frac{S}{\hbar}|A_{cc}(k_0)|=160\text{ Mc/s}$$

$$\left(\frac{S}{\hbar}\right)^2\frac{|A_{xx}(k_0)|^2+|A_{yy}(k_0)|^2}{2}=(68\text{ Mc/s})^2 \tag{17}$$

where $S=5/2$.

To obtain line width formulae which are asymptotically correct as $T\to T_c$, it will be sufficient to express the wavelength dependent susceptibilities $\chi(k)$ in a form valid near the antiferromagnetic mode k_0. Letting $k=k_0+q$ where $|q|\ll k_0$, the molecular field approximation yields the following results above T_c:

$$\chi_{\parallel}(k_0+q)=\frac{g^2\mu_B^2S(S+1)}{3k_BT_c}\frac{1}{\delta+\frac{1}{8}[a^2(q_a^2+q_{a'}^2)+c^2q_c^2]}. \tag{18}$$

Here a and c refer to the unit cell dimensions, and

$$\delta=\frac{T-T_c}{T_c}.$$

Also

$$\chi_{\perp}(k_0+q)=\frac{g^2\mu_B^2S(S+1)}{3k_BT_c}$$
$$\frac{1}{\delta+\delta_{\text{anis.}}+\frac{1}{8}[a^2(q_a^2+q_{a'}^2)+c^2q_c^2]}, \tag{19}$$

where $\delta_{\text{anis.}}=0.02$ is roughly the ratio of the dipolar anisotropy energy to the exchange energy. Note that $\chi_{\perp}(k_0)$ does not diverge at T_c, while $\chi_{\parallel}(k_0)$ does.

Using (17), (18), and (19) in (16), the temperature dependence of the line widths is found to be asymptotically

$$\delta\nu_c=\frac{1}{\lambda}\frac{4}{3}\sqrt{\frac{2}{3}}S(S+1)\frac{|A_{cc}(k_0)|^2}{\hbar^2}$$
$$[\delta^{-1/2}+0.18(\delta+\delta_{\text{anis}})^{-1/2}]$$

$$\delta\nu_a=\frac{1}{\lambda}\frac{4}{3}\sqrt{\frac{2}{3}}S(S+1)\frac{|A_{cc}(k_0)|^2}{\hbar^2}$$
$$[\tfrac{1}{2}\delta^{-1/2}+0.26(\delta+\delta_{\text{anis}})^{-1/2}]. \tag{20}$$

The quantity λ, which we regard as an adjustable parameter, is now chosen to fit the line width data for $T_c+0.015\text{ °K}<T<T_c+1\text{ °K}$. We find

$$\lambda=2.7\times10^{12}\text{ sec}^{-1}. \tag{21}$$

The fit is shown in figure 2, the solid lines corresponding to eq (20). Some deviation in the fit is apparent above T_c+1 °K. This is attributable to the use of the approximate expression (18) and (19) and the replacement of $\mathbf{A}(k)$ by $\mathbf{A}(k_0)$ in (16). Both approximations tend to underestimate the line width at temperatures where contributions from modes k not very close to k_0 become important.

A more serious defect in the theory occurs in the immediate vicinity of T_c where eq (20) predicts divergent line widths proportional to $\delta^{-1/2}$. This contrasts to the constant experimental values reported in eq (2). The infinity in the theory arises from the divergence at T_c of the staggered susceptibility $\chi_{\parallel}(k_0, T)$. We now suggest that in reality this quantity does not become infinite at T_c, but is merely very large over some narrow range of temperatures centered on T_c. In other words we suggest that the critical point is not perfectly sharp, there being a distribution of critical temperatures of width δT_c. Such a situation might well arise when on account of crystalline strains, different parts of the sample have different Curie points. We do not wish to assert that this is really the source of the broadening, however. In any case, a distribution of Curie points should lead to two other experimentally observable effects near T_c:

(1) There should be a coexistence region in which nuclear resonances corresponding to both the paramagnetic and antiferromagnetic phases are simultaneously observable.

(2) The NMR lines observed in the antiferromagnetic state $T<T_c$ should be inhomogeneously broadened. The line width should be maximum when the average local field is along c and minimum when along a. Furthermore, the anisotropy factor $\delta\nu_{\max}/\delta\nu_{\min}$ should be greater than the 2:1 ratio associated with line broadening by fluctuating fields.

Both of these effects were observed and both were consistent with a Curie point distribution of width

$$\delta T_c\cong17\text{ millidegrees}. \tag{22}$$

We now show that such a distribution would result in a finite observed line width at the (average) Curie point $\overline{T}_c$, and we calculate this width. At that temperature, the observed line corresponding to the paramagnetic phase will be due to those members of the distribution which have Curie points T_c somewhat below $\overline{T}_c$. The larger the difference $\overline{T}_c-T_c$, the narrower and hence the stronger will be the contributed NMR line. Roughly speaking, the observed line should then be due to those members of the distribution for which $\overline{T}_c-T_c\cong\frac{1}{2}\delta T_c$. The observed line width should then be given by (20) by inserting the value

$$\delta=\frac{\frac{1}{2}\delta T_c}{T_c}=1.3\times10^{-4}.$$

When this is done, using for λ the value given in (21) we find

$$\delta\nu_c=1200\text{ kc/s}$$
$$\delta\nu_a=600\text{ kc/s} \tag{23}$$

in agreement with the experimental values reported in eq 2. The theoretical line width curves in figure 2 have been "leveled off" at the values (23) just calculated. Thus the divergent theoretical formulae, when modified for the experimentally observed Curie point distribution, yield a good account of the line width broadening above T_c.

Let us see whether our model eq (10) for the relaxation rates is still valid well above the critical point. For $T\gg T_c$, $\chi(k)=\chi_{\text{Curie}}$ and hence $\Gamma(k)=\lambda$ for all k. Then the decay rate for the single-ion correlation functions is also λ. This enables us to compute λ from the F^{19} line width observed at high temperatures [9],

$$\delta\nu_x=170\text{ kc/s}.$$

The result is

$$\lambda=1.8\times10^{12}\text{ sec}^{-1}. \tag{24}$$

Comparing this with the result (21) deduced from the critical fluctuations, we see that the model eq (10) gives a satisfactory picture of the line width behavior above T_c.

We now turn briefly to the situation below T_c, where the line width data is shown by the experimental points in figure 3. In the antiferromagnetic state, the average local field at the nucleus $\mathbf{H}_{\text{NUCL}}$ is the resultant of the applied field and the field produced at the nucleus by the antiferromagnetically ordered Mn^{++} spins:

$$\mathbf{H}_{\text{NUCL}}=\mathbf{H}_0+\mathbf{H}_{Mn^{++}}.$$

Most of the observations were made with $\mathbf{H}_0$ and hence $\mathbf{H}_{\text{NUCL}}$ along c. Some observations were made with $\mathbf{H}_0$ so oriented that $\mathbf{H}_{\text{NUCL}}$ was along a.

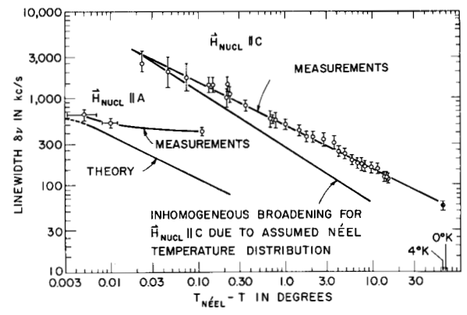

FIGURE 3. *Experimental* F^{19} *line widths below* T_c.
Curves drawn through experimental points represent smoothed data. Other drawn curves represent theoretically calculated line width for $\mathbf{H}_{\text{NUCL}}$ along a and inhomogeneous broadening with $\mathbf{H}_{\text{NUCL}}$ along c, calculated for a Curie point distribution of width $\delta T_c=17$ mdeg.

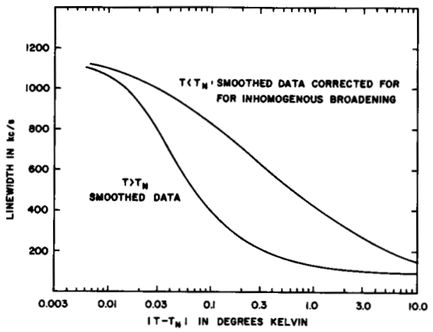

FIGURE 4. *Line widths for* $\mathbf{H}_{\mathrm{NUCL}}$ *along* c *above and below* T_c. Line widths for $T < T_c$ have been corrected for the inhomogeneous broadening due to the Curie point distribution.

When this condition was satisfied the NMR lines were quite narrow. This is because the inhomogeneous field $\Delta\mathbf{H}$ arising from the distribution of Curie points is along c; only a second order broadening results with $\mathbf{H}_{\mathrm{NUCL}}$ perpendicular to $\Delta\mathbf{H}$.

An upper bound on the second order inhomogeneous broadening for $\mathbf{H}_{\mathrm{NUCL}}$ along a was calculated by postulating that all of the observed broadening for $\mathbf{H}_{\mathrm{NUCL}}$ along c was inhomogeneous. This upper bound was considerably smaller than the line width $\delta\nu_a$ observed for $\mathbf{H}_{\mathrm{NUCL}}$ along a. We conclude that the $\delta\nu_a$ line widths shown in figure 3 do not reflect the inhomogeneous broadening. They are due presumably to fluctuations.

It was possible roughly to correct the data for $\mathbf{H}_{\mathrm{NUCL}}$ along c for the inhomogeneous broadening. This was done in two ways as follows:

(1) The corrected value of $\delta\nu_c$ was set equal to twice $\delta\nu_a$ at those temperatures where the $\delta\nu_a$ data was available.

(2) Assuming that the $\delta\nu_c$ line widths observed just below T_c were entirely inhomogeneous, the width of the Curie point distribution was found to be about 17 mdeg. Then the inhomogeneous part of the broadening was calculated as a function of temperature and "subtracted off" from the observed line width.

The estimated line width for $\mathbf{H}_{\mathrm{NUCL}}$ along c, corrected for the inhomogeneous broadening is shown as a function of $|T_c - T|$ in figure 4, together with the actual $\delta\nu_c$ line widths for $T > T_c$. Note that the corrected line width is continuous at T_c.

The theory described above, which gave a satisfactory account of the behavior above T_c, can be used to calculate the line widths for $T < T_c$. Using the molecular field model to calculate the wavelength dependent susceptibilities, the theoretically calculated line width is found to fall off much more rapidly with decreasing temperature than the experimentally observed width. This discrepancy is illustrated in figure 3, where the theoretical line width for $\mathbf{H}_{\mathrm{NUCL}}$ along a is compared with the data. At present, therefore, we do not understand the line width behavior below T_c.

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References

[1] P. Heller and G. B. Benedek, Phys. Rev. Letters **8**, 428 (1962).
[2] P. Heller and G. B. Benedek, Phys. Rev. Letters **14**, 71 (1965).
[3] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).
[4] T. Moriya, Prog. Theor. Phys. **16**, 23, 641 (1956).
[5] T. Moriya, Prog. Theor. Phys. **28**, 371 (1962).
[6] H. Mori and K. Kawasaki, Prog. Theor. Phys. **25**, 723 (1962).
[7] P. Heller, Thesis, Harvard University 1963 (unpublished).
[8] A. M. Clogston, J. P. Gordon, V. Jaccarino, M. Peter, and L. R. Walker, Phys. Rev. **117**, 1222 (1960).
[9] R. G. Shulman and V. Jaccarino, Phys. Rev. **108**, 1219 (1956).

Discussion

G. S. Rushbrooke: May I ask Dr. Domb how summing over further graphs besides ring graphs differs fundamentally from applying say the Percus-Yevick equation to the Ising model, which one knows is not very good?

C. Domb: The approximation which I propose attempts to find an asymptotic representation of polygons and other graphs on the lattice. In terms of Mayer theory it corresponds to summing *all* cluster integrals which can be formed using all the bonds of these configurations on the lattice. Thus even in lowest order when it is concerned only with polygons it still takes into account a much more complex set of integrals than those of simple ring type. In this respect the lowest order approximation is the generalization to infinity of the ring approximation of Rushbrooke and Scoins. It seems to me that approximations like those of Percus-Yevick are derived by summing *Mayer* ring integrals, and make no serious attempt to estimate asymptotically the number of polygons on the lattice and the corresponding excluded volume effect.

M. E. Fisher: I would like to make a comment on the point that Dr. Rushbrooke raised. It is in the spirit of the Van der Waals equation to take into account the short range repulsion exactly. The short range repulsion with excluded volume effects is also a difficult problem, but the point is that it is possible to split the problem this way. This approach using the data from lattice models represents it, one hopes, in a better way.

C. N. Yang: Dr. Domb said he believed that for some three dimensional lattice models the specific heat singularities below the critical temperature are logarithmic. What is the constant in front of the logarithm?

C. Domb: Unfortunately, I have not got the figures at this moment, but I can easily provide them at a later stage.

B. R. Livesay presented measurements of the magnetization of thin nickel films near the Curie temperature [1].

J. C. Eisenstein: I would like to report some measurements on $NdCl_3$, which have been carried out by Hudson and Mangum here at the National Bureau of Standards [2]. This substance has highly anomalous magnetic properties. It has two extremely sharp spikes in its susceptibility at approximately 1.0 and 1.7 °K. With regard to the dependence of the susceptibility on the temperature in the vicinity of the 1.7 °K peak, we found that the coefficients γ and γ' are approximately the same. However, they are not 1.3, but approximately 0.69. Also the susceptibility of $CeCl_3$ was measured [3]. It was found that the susceptibility of this substance has a very sharp spike at 0.345 °K. We think $CeCl_3$ has a second susceptibility peak at a lower temperature, but it has not been located yet. For $CeCl_3$ the value of γ on the high side of the transition is about 0.61. The measurements on $NdCl_3$ extended from about 5 to 55 mdeg on either side of the transition. For $CeCl_3$ the range was 10 to 100 mdeg.

E. Callen: There exists some theoretical analysis of the Heisenberg Hamiltonian. If one looks for the asymptotic behavior, any cluster theory or Green's function theories give the value $\beta = 1/2$. That is in

$$M = D(1 - T/T_c)^{\beta} \tag{1}$$

the behavior of M *asymptotically* at $T = T_c$ is given by $\beta = 1/2$. On the other hand, however, if one is content with some sort of a numerical procedure, it turns out that many results are already given by simple models. In particular, if one carries out the variational procedure as described by Dr. Livesay, in which one considers dM/dT as a function of β and takes the value of β which gives the best fit to the magnetization curve, the Green's function theories give $\beta = 1/3$ for a broad temperature range. Also the cluster theory including nearest-neighbor and next-nearest-neighbor interaction leads to the 1/3 power [4]. Furthermore, by taking the nearest and next-nearest exchange constant from experimental data without using any adjustable parameter, the cluster theory predicts the observed value of the coefficient D in (1) within 2 percent. Although these theories are not correct asymptotically at $T = T_c$, numerically one obtains rather good results from the present existing theory away from T_c. Perhaps only higher and higher sophistication will extend this range of validity to temperatures closer and closer to T_c.

H. B. Callen: I would like to amplify that. There has been a great deal of discussion, it seems to me, about rigorous theories. Nevertheless, the molecular field theory, the cluster theory and other phenomenological theories have historically turned out to be very convenient. These theories to my mind have not been considered sufficiently in the discussion so far. As my brother just observed, they are in fact considerably more successful than they have been given credit for. I would like to review very rapidly some of the successes these theories have had, choosing specifically a form of Green's function theory.

If one asks for the equation of motion of a spinwave, one has to take into account the interaction between two spinwaves. This interaction is described by the appearance of S_z in the Hamiltonian [5]. Now one can represent S_z in either of the following two forms [5]:

$$S_z = S - S^- S^+ \tag{2}$$

or

$$S_z = \tfrac{1}{2}(S^+ S^- - S^- S^+) \tag{3}$$

As the averages are calculated by some kind of approximation the two methods do not lead to the same result. However it is possible to make a guess as to which of the two methods is better at low temperature and which one better at high temperature. One therefore introduces a parameter and says that the total S_z is a linear combination of (2) and (3), the ratio being $(\frac{1}{2}S)^x(S_z/S)^x$. This has been investigated for various values of the exponent x. At first we [5] had carried out the method for $x = 1$ but at the meeting in Kansas City in March 1965 Copeland and Gersch indicated that they had investigated the method for general x, and that for $x = 3$ the theory leads to excellent results [6]. For the shape of the critical isotherm, Copeland and Gersch reported $\delta = 4.22$, whereas various experiments that have been reported here give $\delta = 4.2 \pm 0.2$. For the coefficient of the susceptibility above the Curie temperature they reported $\gamma = 4/3$ quite accurately. As my brother told you, all Green's function theories give $\beta = 1/3$, but only at some distance below the Curie temperature (much further below than Dr. Benedek found). In fact, one finds that the value of β changes from 1/2 close to the Curie temperature to $\beta = 1/3$ some distance away from the critical temperature. Incidentally this is very reminiscent of the data in He^3 that Dr. Sherman presented, where they found experimentally a narrow region where the coexistence curve follows a 1/2-power law going over into a 1/3-power law beyond this region. Finally, I remind you that the coefficient D in (1) is correctly predicted to within 2 percent.

Anonymous: How is the value 3 chosen for the exponent x?

M. E. Fisher: By comparison with experiment?

H. B. Callen: Copeland and Gersch find the magnetization to be double valued if one takes x in the range $1 < x < 3$. The selection of $x = 3$, rather than $x > 3$, is on the ad-hoc basis of the results cited.

G. E. Uhlenbeck: I would like to make a comment with regard to the remarks of Dr. Callen. I am not in favor of saying that the theories you mentioned have not led to interesting results. However, I do not think it is right to treat them on the same level as the classical theory. The classical theory corresponds to a definite model namely long range forces, while the theories you mentioned contain what I would call uncontrolled approximations.

H. B. Callen: At the risk of a rebuttal which may call forth another rebuttal, I remark that the molecular field theory only became an exact model many years after it was phenomenological. That is, the model for which it is exact was not discovered until long after the theory has been presented. I imagine that for any so called phenomenological model, one can find, if one is clever enough, some obscure model for which it is a rigorous solution. In the case of the molecular field solution one contrives a model in which every spin interacts equally strongly with every other spin. It seems to me to be a technicality to call that a physical model, and to make a distinction between that theory and other phenomenological theories.

L. Tisza: The internal field theories can be discussed from two points of view and these are not in conflict if properly distinguished. We may search for models or types of interactions for which such a theory is more or less adequate, or else, we may consider the method as an approximation to the real state of matters and observe its point of breakdown. I wish to make a remark from the second point of view. It is possible to formulate the statistical thermodynamics of equilibrium in a fashion that a finite system appears to be coupled with its infinite environment. The system is specified by additive random variables the distribution of which contains the intensities of the environment as parameters. The theory is still valid for small systems, but it fails for critical points where an important Jacobian vanishes [7]. This argument justifies the use of an internal field as the intensity of the environment of a small open system, independently whether the interaction is of short or long range. However, the theory fails near the critical point and here more incisive methods have to take over.