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Jerome F. Siebert

March 1968
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ELECTRON RESONANCE STUDIES OF CRITICAL FLUCTUATIONS IN ANTIFERROMAGNETS

Jerome F. Siebert

(Ph.D. Thesis)

March 1968
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Magnetic relaxation in the three antiferromagnets CsMnF$_3$, RbMnF$_3$, and K MnF$_3$ has been studied as a function of temperature, with special emphasis on the critical region just above $T_N$. CsMnF$_3$ ($T_N \approx 53^\circ$K) has a large dipolar anisotropy which makes the basal plane an easy plane, so that the position of the low frequency mode depends only on the magnitude of the applied field. It was therefore possible to make a detailed, continuous study of the AFR-EPR transition in this crystal without using the high field or high frequency techniques ordinarily required to observing AFR in anisotropic antiferromagnets. A large broadening of the line width was observed immediately above $T_N$, as predicted by the conventional theory of critical fluctuations. However, the broadening was asymmetric, suggesting that the intrinsic spin relaxation is masked by inhomogeneous broadening and sample-dependent effects. An anomalous line width "hump" in the AFR region can also be attributed to such effects. Since the external field partially polarizes the sample, the presence of anisotropy produces a shift in the resonance field, even in the paramagnetic region. The resonance fields in CsMnF$_3$ were measured as a function of temperature between 75$^\circ$K and 300$^\circ$K with the field applied parallel and perpendicular to the c-axis. The results were qualitatively consistent with the behavior and temperature dependence of the anisotropy field predicted by theory and determined from low temperature torsion experiments. However,
quantitative agreement could be obtained, especially at the lower temperatures. 

$\text{RbMnF}_3 \ (T_N \approx 82.5^\circ \text{K})$ and $\text{K MnF}_3 \ (T_N \approx 88^\circ \text{K})$ are low anisotropy, cubic antiferromagnets, so that intrinsic spin processes should dominate the relaxation. In both crystals the linewidth remained constant as the temperature was lowered from room temperature through $T_N$. This result is inconsistent with existing theories of spin relaxation based on the conventional theory of critical fluctuations. Therefore, a critical review of these theories was made and some possible modifications are proposed that will produce better agreement between theory and experiment. For instance, conventional theories do not consider the effect on spin relaxation of collective oscillations above $T_N$, i.e., "para-magnons," whose existence has recently been established experimentally in $\text{RbMnF}_3$. For completeness, this modified theory of spin relaxation is extended to the case of anisotropic antiferromagnets and compared with experiment.
I. INTRODUCTION

The magnetic behavior of a system at temperatures in the vicinity of its transition temperature has been the subject of considerable interest in recent years. As is well known, conventional thermodynamics predicts anomalous increases in the time and spatial correlation of the electronic spin arrangement as the transition temperature is approached from above. Therefore, considerable insight into the nature of the ordering process can be obtained from a careful study of these so-called critical fluctuations.

Usually, interest is centered on the form and temperature dependence of the time-dependent, spin correlation functions

\[ \rho_{\alpha\beta}(R_{ij}, t) = \langle S_i^\alpha(t), S_j^\beta(0) \rangle, \quad (1) \]

relating the components \((\alpha, \beta)\) of pairs of spins separated by a distance \(R_{ij}\) and a time \(t\), where \(\langle \rangle\) means the thermal average and \((A,B) = (AB + BA)/2\). Perhaps the most direct information on these pair correlation functions can be obtained from the critical scattering of thermal neutrons close to elastic Bragg peaks. Furthermore, in these experiments it is possible to observe the time and spatial correlation separately. Until recently, most neutron experiments have dealt exclusively with the problems of spatial correlation, and have well-verified the general prediction that there are anomalous increases in local order near a magnetic transition. Since conventional thermodynamics predicts correlation in time and space should increase together, it was, therefore, quite surprising when recent neutron experiments indicated that there were no corresponding increases in the time
correlation of the spins near the transition. 1 Unfortunately, the time correlation experiments were limited by resolution difficulties, which prevented a detailed look at this problem until very recently. The situation was further complicated by the results of nuclear magnetic resonance (NMR) line width studies on magnetic crystals in the critical region. Moriya 2 has shown that NMR line widths in magnetic systems can be directly related to the time correlation of the electron spins. Using this theory, Heller 3 was able to interpret NMR line width measurements made on MnF 2 near T N by assuming conventional behavior for the time correlation of the spins, in apparent contradiction with the neutron results. Clearly, further studies, both experimental and theoretical, were needed on the general problem of time correlation in magnetic systems.

In this paper we report the results of recent experimental determinations of the temperature dependence of the electron resonance (EPR) line width in the critical region in certain antiferromagnets. As in the NMR case, we expect that the EPR lines will reflect increases in spin correlation, and therefore can be used to indirectly study the behavior of F 02(R ij,t). In particular, it is well known that the presence of a large exchange interaction will considerably narrow the resonance absorption, so that the effect of exchange on the spin motion and correlation can be directly related to the line width of the absorption. However, this relation is considerably more complicated than in the NMR case. To make the study complete we have considered both isotropic and anisotropic antiferromagnets. The importance of understanding the anisotropic case is illustrated by the following two facts:

1 EPR line width singularities have been observed only in anisotropic
antiferromagnets; and (2) NMR studies have been made only on anisotropic MnF$_2$, while to date careful neutron studies of time correlation have been made only on isotropic systems. Therefore, the presence of anisotropy may well be an important factor in understanding the apparent contradiction between the NMR and neutron results for electronic time correlation near a magnetic transition.

For these experiments we chose the three antiferromagnets CsMnF$_3$, RbMnF$_3$, and KMnF$_3$. Since Mn$^{++}$ is an S-state ion, the transverse magnetic relaxation is due entirely to spin-spin interactions, and therefore these crystals are ideal for resonance studies of spin correlation in the critical region. Their magnetic and crystallographic properties are discussed in Sec. III.

CsMnF$_3$, a hexagonal hard-axis antiferromagnet, seemed an ideal choice for these studies for several reasons: (1) considerable work has been done on this crystal at low temperatures so that its magnetic and crystallographic properties are reasonably well established; (2) since it is a hard-axis antiferromagnet, it was possible to continuously observe the low frequency resonance mode through the transition without resorting to the high frequency or high field techniques ordinarily required to follow the resonance in anisotropic antiferromagnets below $T_N$; and (3) it offers a useful contrast to MnF$_2$, which is an easy-axis antiferromagnet whose electron resonance properties have already been studied in the critical region. However, the properties of CsMnF$_3$ proved to be far more complicated near the critical point than anticipated. In particular, we found that asymmetric broadenings and narrowings of the resonance line completely dominated the resonance behavior in the critical region. Furthermore, there was some evidence
that the Néel temperature might not be well defined. In view of this, we were not able to use these results to help clarify the general problem of spin correlation near a magnetic transition. Consequently, the results of this experiment are considered separately in Sec. IV, together with a qualitative discussion of the unusual line width and resonance field behavior of this crystal.

In Sec. V we discuss in detail the experimental results on the cubic antiferromagnets RbMnF₃ and KMnF₃. Although there is no line width anomaly (the line width remains constant from room temperature down through the transition in both crystals), these results offer an excellent opportunity for testing the general theories of spin relaxation in isotropic antiferromagnets near $T_N$. Since these theories are not well established there is considerable speculation in this section. However, we do come to the conclusion, consistent with the neutron results, that the time correlation of the spins does not increase anomalously in these crystals near $T_N$. Recently Marshall showed that the presence of collective oscillations above $T_N$ (i.e., "para-magnons") will produce additional motion of the spins, not considered by the conventional theory, that could account for this behavior. The existence of such oscillations above $T_N$ has been recently verified by high resolution neutron experiments on RbMnF₃. Therefore, a modification of our theory of spin damping to include the effects of para-magnons produces much better agreement between theory and experiment. Also, if we consider the effect of anisotropy on the existence of para-magnons, it is possible to understand the conventional behavior of the time correlation observed in MnF₂. However, even with these modifications, agreement between theory and experiment is far from satisfactory.
In Sec. VI we have extended this modified theory of spin relaxation to anisotropic antiferromagnets, and illustrate how a line width singularity in these crystals can be attributed to the combined effect of anisotropy and spatial correlation. This result is consistent with the characteristic line width singularity observed in all anisotropic antiferromagnets in the critical region.
II. EXPERIMENT

A. Apparatus

A standard Q-band (26.5 → 40 Ge) spectrometer of the conventional magic-T design was used for most of the experiments. The Zeeman field was modulated at 320 cps in order to permit A.C. amplification of the resonance signal, and therefore, the phase-detected signal was a close approximation to the derivative of the resonance absorption. Derivative signals are usually preferred for the measurement of line widths and g-values, particularly broad lines, since it is not as difficult to establish the baseline and resonance maximum as it is in the case of pure absorption measurements. Line widths in CsMnF₃ ranging from 100 Oe to over 4000 Oe were observed with little difficulty in this manner.

The major experimental problem proved to be temperature control of the sample. It was decided to thermally isolate the sample from the resonance cavity so that the sample temperature could be varied independently. An assembly drawing of the cavity and temperature control unit is shown in Fig. 1. The sample is placed very near a small hole in the end-wall of a rectangular cavity resonating in the TE₁₀₁ mode. The electron spins see the microwave field that "bulges" through this hole, and therefore, from an electromagnetic point of view, the sample is effectively inside the cavity. (This is a reasonable assumption only if the sample size and distance from the hole are kept on the order of the hole diameter.) The sample is supported by a copper barrel containing a platinum resistance thermometer wrapped with a fine manganin heater wire. Apiezon N-grease was used to mount the sample and to improve thermal contact between all independent parts.
Finally, the copper barrel is supported by three thin brass struts attached to the cavity. Therefore, when the entire assembly is sealed inside a vacuum tight can, the only significant thermal contact between the cavity and the sample is along the struts. With the resistance thermometer as one arm of an A.C. bridge and a phase-sensitive detector to drive both a current amplifier and a servo-motor, an equilibrium temperature gradient could be rapidly established along the brass struts. With helium as the coolant this system is capable of controlling the sample temperature to better than a millidegree over the range 200K to 1000K. By using different coolants, temperature control of at least ± 0.010K can be obtained over the range 10K to 3000K. Since the resistance thermometer was uncalibrated, a reference temperature accurate to ± 0.10K was established in the temperature region of interest with a copper-constantan thermocouple; then relative temperatures accurate to a millidegree could be established within a 5 degree range by using published tables for the temperature dependence of the resistance of platinum. In the same manner, errors due to the temperature gradient between the sample and the resistance thermometer were systematically eliminated.

B. Samples

Two high quality single crystals of CsMnF₃ were available for these experiments. The first, crystal I, was a small chip that had been sandblasted off a large single crystal with a sharply collimated beam of aluminum oxide microparticles. Both the size and experimental behavior of the large crystal, which was supplied by Dr. R. W. H. Stevenson of the University of Aberdeen, were indicative of its high quality. Uncollimated x ray photographs of the chip showed no evidence
of strain. Crystal II, which also appeared unstrained, was grown by K. Lee and had been polished to a smooth sphere approximately .030" in diameter. The remainder of the experiments were carried out on single crystal chips of RbMnF$_3$ and KInF$_3$ that were obtained from Semi-Elements, Inc. These crystals showed some evidence of strain, and were, in general, of lesser quality.

III. MAGNETIC AND CRYSTALLOGRAPHIC PROPERTIES

A. RbMnF$_3$

RbMnF$_3$ has the ideal perovskite structure with the Mn$^{++}$ ions forming a simple cubic lattice with spacing 4.24 Å and remains undistorted at all temperatures.$^{11,12}$ Below $T_N \approx 82.5^0 K$ the system orders antiferromagnetically with the spins alternating in direction along a cube edge. The exchange interaction is essentially between nearest neighbors ($H_e \approx 9 \times 10^5$ Oe) and its magnetic anisotropy is extremely weak ($H_a \approx 5$ Oe). Therefore, RbMnF$_3$ is an excellent approximation to the ideal cubic Heisenberg antiferromagnet.

Because of the weak anisotropy the spin-flop field$^{13}$ is low (i.e., $H_c \approx (2H_eH_a)^{1/2} \approx 3 \times 10^3$ Oe at $T = 0$), so that for the high resonance fields of this experiment ($H_o \approx 10^4$ Oe) the sublattice magnetizations are essentially perpendicular to the applied field for all crystal orientations. Then the resonance frequencies at $T = 0$ can be written

$$ (\omega/\gamma)^2 \approx [2H_eH_a + H_o^2] \quad (2) $$

$$ (\omega/\gamma)^2 \approx [2H_eH_a] \quad (3) $$

Since the molecular field approximation predicts $(2H_eH_a)^{1/2} \propto M$, we expect that $(2H_eH_a)^{1/2} << H_o$ close to $T_N$, so that the resonance frequency
as determined by Eq. (2) is insensitive to the magnetic phase transition. The resonance mode described by Eq. (3) is field independent and therefore could not be observed with a field modulation experiment.

B. K\textsubscript{MnF\textsubscript{3}}

K\textsubscript{MnF\textsubscript{3}} is also cubic perovskite at room temperature with lattice spacing 4.19 Å, but distorts slightly at 184°K to an orthorhombic phase with a twinned structure.

A further structural change is reported to occur at \( T_N \approx 85°K \), below which the pseudocell is again orthorhombic, but with different cell dimensions. Finally, a second magnetic transition occurs at 81.5°K with distortions that give rise to canting interactions and weak ferromagnetism.

Despite these distortions, the magnetic properties of K\textsubscript{MnF\textsubscript{3}} near \( T_N \) are quite similar to those of Rb\textsubscript{MnF\textsubscript{3}}. Essentially a nearest neighbor exchange interaction (\( H_e \approx 1.6 \times 10^6 \) Oe) causes the spins to alternate in direction along a cube edge in the ordered region, and there is a very weak anisotropy (\( H_a \approx 4 \) Oe). Therefore, the resonance modes are also described by Eqs. (2) and (3), and we expect qualitatively the same critical behavior in both crystals as the transition temperature is approached from above.

C. Cs\textsubscript{MnF\textsubscript{3}}

The crystal structure of Cs\textsubscript{MnF\textsubscript{3}} is the same as the hexagonal form of Ba\textsubscript{TiO\textsubscript{3}}. Fig. 2 shows one-half of the unit cell, which has the dimensions \( a = 6.213 \pm 0.003 \) Å and \( c = 15.074 \pm 0.004 \) Å. A complicating feature of this structure is that there are two inequivalent magnetic sites. One third of the manganese sites (denoted Mn\textsubscript{1}) are surrounded by fluorines having one type of distortion, and the remaining two thirds are surrounded by fluorines having two different
distortions. The Mn\textsubscript{1} sites have six nearest neighbors of type Mn\textsubscript{2}, while the Mn\textsubscript{2} sites have three nearest neighbors of type Mn\textsubscript{1} and one of type Mn\textsubscript{2}. Within the basal plane each site has six next nearest neighbors of the same type.

Low temperature torsion and susceptibility measurements\textsuperscript{16} indicate a transition to the antiferromagnetically ordered state at 53.5°K due to an effective exchange field $H_e \approx 3.5 \times 10^5$ Oe, and establish the existence of a large uniaxial anisotropy which makes the basal plane an easy plane ($H_a \approx 7.5 \times 10^3$ Oe). Anisotropy in the basal plane is essentially zero, so that the preferred direction of the spins is established by the direction of the external field. As a result, the electron spins are always perpendicular to the applied field regardless of the field direction. The spins lie perpendicular to the hexagonal c-axis in ferromagnetic planes. These ferromagnetic planes, which contain only one type of manganese site, are stacked antiferromagnetically along the c-axis. This stacking may be denoted by A(+), B(−), B(+), A(−), C(+), C(−), A(+), where (+) and (−) refer to the electron spin direction in space, A refers to a Mn\textsubscript{1} type of ferromagnetic plane, and B and C refer to Mn\textsubscript{2} type ferromagnetic planes. Therefore, the magnetic structure of CsMnF\textsubscript{3} is quite complicated (six-sublattices) and we might expect similar complications in its dynamic behavior. However, it is useful to make the molecular field approximation of a two-sublattice antiferromagnet in order to get a qualitative picture of the resonance modes of this system. This has been done by Lee et al.\textsuperscript{16} who found for $T = 0$

$$\left(\frac{\omega}{\gamma}\right)^2 = \frac{1}{2} H_o^2 + H_e H_a \pm \left[\left(\frac{H_e H_a}{2} + \frac{1}{2} H_o^2\right)^{\frac{1}{2}} - 2 H_e H_a H_o^2 \sin^2 \theta\right]^{\frac{1}{2}}$$  (4)
where $\theta$ is the angle between the applied field and the anisotropy axis, and we have ignored the hyperfine interaction. The two crystal orientations of major interest are with the field parallel and perpendicular to the anisotropy axis. For these cases the resonance frequencies are

\[
(\omega/\gamma)^2 = 0, \quad [2H_e H_a + H_0^2] \quad \theta = 0, \tag{5}
\]

\[
(\omega/\gamma)^2 = H_0^2, \quad 2H_e H_a \quad \theta = \pi/2. \tag{6}
\]

For each orientation there is one field dependent resonance mode, which is the only one we can observe experimentally because of field modulation. These field dependent modes are shown in Fig. 3. In the following section the actual experimental behavior of these modes is discussed in detail.

IV. RESONANCE PROPERTIES OF CaMnF$_3$

A. Experimental results

Low Frequency Mode ($\theta = \pi/2$)

With the external field in the easy plane Eq. (6) predicts the resonance frequency depends only on $H_0$, and is therefore insensitive to the magnetic transition. As a result it was possible to observe the EPR - AFR transition continuously with a standard constant frequency spectrometer, without resorting to the high frequency or high field techniques ordinarily required to follow the resonance in anisotropic antiferromagnets below $T_N^\perp$. The temperature dependence of the low frequency resonance line width $\Delta H$ of crystal I from 4$^\circ$K to 300$^\circ$K is shown in Fig. 4. ($\Delta H$ is defined as the distance between the peaks of the
derivative resonance curve.) There is a sharp, but finite singularity near the predicted transition temperature, and surprisingly, a large "hump" in the AFR region. The details of the singularity are shown in Fig. 5 where we have also shown the corresponding temperature dependence of the mean resonance field. Since Eq. (6) predicts a temperature independent resonance field, this latter behavior is unexpected. There also appears to be considerable correlation between this field and the line width. Below $T = 51.85^\circ\text{K}$ the resonance field curve closely resembles the derivative of the line width curve, while above this temperature the behavior of the curves is almost identical. The reason for this correlation is illustrated by Fig. 6, which shows three superimposed derivative curves taken at different temperatures above $T = 51.85^\circ\text{K}$. The lines are clearly broadening in an asymmetric manner such that the low-field side moves downfield while the high-field side remains essentially at fixed field. If we go to lower temperatures the roles of the low-field and high-field sides reverse periodically (i.e., sometimes the low-field side remains fixed while the high-field side moves), so that the temperature dependence of the resonance field between $40^\circ\text{K}$ and $60^\circ\text{K}$ can be almost entirely attributed to these asymmetric broadenings and narrowings of the resonance line.

Since asymmetric broadenings often imply corresponding changes in the resonance line shape, then the plot of $\Delta H$ in Fig. 5 might be misleading. This is because the parameter of theoretical interest is the half-width at half-maximum of the resonance absorption (defined as $(1/\gamma T_2)$), and not the distance between peaks $\Delta H$ of its derivative curve. For a given line shape these parameters are proportional, but the proportionality constant changes with the shape. For instance, if the
curve were Lorentzian then \( \frac{1}{\gamma T_2} = (\sqrt{3}/2)\Delta H \), but if the curve were Gaussian \( \frac{1}{\gamma T_2} = (2\pi)^{-1/2} \Delta H \). Then it is possible that \( \frac{1}{\gamma T_2} \) could decrease as \( \Delta H \) increases (or vice versa) in the critical region because of the distorting line shape. In particular, it is uncertain whether the peak in \( \Delta H \) corresponds to the peak in \( \frac{1}{\gamma T_2} \) that defines \( T_N \), so that perhaps a better choice for \( T_N \) is the inflection point at \( T = 51.85^\circ K \), or even some other temperature. This problem could have been avoided to some extent by making pure absorption measurements, but the broad lines and correspondingly small signals made this unfeasible. Furthermore, the very existence of asymmetric distortions suggests that the critical point in \( \text{CaMnF}_3 \) may not be well defined in the first place. This possibility will be considered later in more detail.

Similar experiments were carried out on crystal II with identical results in every respect, except that the line width and resonance curves are shifted approximately \( 1.3^\circ K \) to a higher temperature. That is, the curves of both crystals would exactly overlap if it were not for a uniform shift of the curves of crystal II to a higher temperature. Surprisingly, all crystals of the same origin as crystal II showed approximately the same \( 1.3^\circ K \) shift of the line width singularity with respect to the results of crystal I. If \( T_N \) were very sensitive to purity, strain, etc., a distribution in the position of the singularity would seem more likely. However, it is difficult to imagine other possible reasons for this inconsistency in results. It should also be noted that the torsion experiments\(^{16}\) that established \( T_N \approx 53.5^\circ K \) were carried out on crystals of similar origin as crystal II.
High Frequency Mode ($\theta = 0$)

The critical behavior of the line width with the applied field parallel to the anisotropy axis is also shown in Fig. 5. The behavior in the paramagnetic region is very similar to the corresponding behavior of the low frequency mode. The broadening is asymmetric with the low field side shifting to lower fields, but now this effect is much larger and becomes significant at higher temperatures. The resonance field is indicated at various points along the line width curve. The line broadens continuously through $T = 51.85^0K$ (not shown) and at $T = 51.15^0K$ we find $\Delta H \approx 3500$ Oe and $H_{\text{res}} \approx 6500$ Oe. In this temperature range both peaks of the derivative curve are moving downfield, but the downfield movement of the low-field peak is still more rapid. Also, the rate of broadening with decreasing temperature is gradually slowing down. At still lower temperatures there is almost no more broadening, but the resonance continues to move rapidly downfield and fades in intensity, until for $T \leq 50.15^0K$ it is no longer detectable.

Similar behavior has been observed in RbMnCl$_3$, which is also a hard axis antiferromagnet. In interpreting the resonance behavior of this crystal it was pointed out that the rapid downfield movement and subsequent fadeout of the resonance is the expected behavior of the high frequency mode just below $T_N$. Since from the molecular field approximation we have $(2H_e H_a) \frac{1}{2} \propto M$, then Eq. (5) predicts the applied field required for resonance at fixed frequency will rapidly decrease due to the increasing contribution of $(2H_e H_a) \frac{1}{2}$ as the temperature is lowered below $T_N$. However, no explanations were suggested for the line width behavior above $T_N$. As will be shown in Sec. VI, conventional explanations for the line widths and resonance shifts in CsMnF$_3$ are
inadequate. Although these explanations do predict a broadening of the line widths in the critical region, they do not predict the asymmetric broadenings and narrowings that seem to dominate this resonance behavior. Therefore, in the following section we will make several qualitative suggestions for possible broadening mechanisms that might be responsible for the unusual resonance behavior of CsMnF$_3$ in the critical region.

B. Discussion

In this section we will confine ourselves to a discussion of the three major features of the resonance data: (1) the asymmetric behavior of both modes, especially in the paramagnetic region; (2) the anomalous behavior of the low frequency mode in the immediate vicinity of $T_N$; and (3) the AFR line width "hump" of the low frequency mode. A clue to the asymmetric behavior of the resonance lines in the paramagnetic region is provided by our earlier explanation for the rapid decrease in resonance field of the high frequency mode just below $T_N$. In this explanation we recognize the increasing importance on the resonance frequency of a field $(2H_eH_a)^{\frac{1}{2}}$, due to the rapid growth of long-range order below the transition. Above the transition there is no long-range order, but conventional thermodynamics predicts large fluctuations in local order as the transition temperature is approached from above, so that roughly speaking, we can picture the spin arrangement at any instant of time as clusters of ordered spins. (The theory of critical fluctuations is presented in Sec. V.) Then it is not unreasonable to expect that spins near the center of these clusters will see an additional resonance field due to the local order that is much like the field $(2H_eH_a)^{\frac{1}{2}}$ present below $T_N$. We therefore define a field $H_c$ to describe this effect of local order on the resonance behavior of a given
spin. Then the root-mean-square value of this field \( \bar{H}_c \) is proportional to the average cluster size and the value of \( (2\epsilon H_a)^{\frac{1}{2}} \) at \( T = 0 \). We then write

\[
(\omega/\gamma)_{\text{ave}}^2 \approx [H_0^2 + \bar{H}_c^2] \quad T \approx T_N. \tag{7}
\]

However, the existence of clusters implies spin environments ranging from total order near the center of a cluster to total disorder at the surface. We therefore expect a broad distribution in the local resonance field \( H_c \), so that the resonance absorption should be asymmetrically broadened to lower fields with a width \( \Delta H \approx 2\bar{H}_c \). Qualitatively, this is just the behavior experimentally observed in the high frequency mode above \( T_N \), while the smooth transition of this behavior to temperatures below \( T_N \) (where these arguments are more rigorous) gives further support to this interpretation of the line width.

Since the low frequency mode has a similar behavior in the paramagnetic region, we look for a related explanation. That is, we again postulate the existence of an additional resonance field \( H_c \) due to short range order. However, the origin of such a field is less obvious than in the high frequency case since Eq. (6) predicts that the resonance depends only on \( H_0 \) below \( T_N \). It is possible that a more careful derivation of this frequency, taking into consideration the full complexity of the structure of CsMnF\(_3\), would yield an additional term dependent on long-range order that could explain the origin of \( H_c \).

Another possibility is that the boundary conditions introduced by the finite size of the clusters might considerably modify the anisotropy fields, and therefore change the resonance condition. In any case, if
such a field existed we would expect it to depend on cluster size, etc., in much the same manner as in the high frequency case. In Fig. 7 we have made doubly logarithmic plots of the line widths versus \((T - T_N)\), where we have arbitrarily assumed \(T_N = 51.85^\circ\text{K}\). In spite of this arbitrary choice it is clear that both the low and high frequency modes are broadening at roughly the same rate, which supports the assumption that the broadening mechanism is similar for both modes. However, if we use this argument to relate the relative magnitudes of the low and high frequency mode line widths to the corresponding magnitudes of \(\tilde{H}_c\), then our experimental results predict that \(\tilde{H}_c\) is only a factor of 2 smaller in the low frequency case. It is difficult to imagine how second-order contributions to the resonance condition could lead to such a large effect.

Also, the predictions of this analysis are not entirely consistent with the experimental results on other crystals. For example, \(\text{MnF}_2\) has a resonance condition very similar to Eq. (5), but in spite of extensive experimental work on this crystal in the critical region, there has been no report of such shifts. Resonance shifts to lower fields have been observed in the paramagnetic region of \(\text{RbMnCl}_3\) in experiments at 70 Gc, although they were considerably smaller than in \(\text{CsMnF}_3\). Smaller shifts at higher frequencies might be understood with the following argument. For fixed frequency, Eq. (7) predicts the resonance shift due to an increase in average cluster field \(\tilde{H}_c\) is inversely proportional to the resonance field, i.e.,

\[
\Delta H_o \approx - \left(\frac{\tilde{H}_c}{H_o}\right) \Delta H_c
\]

(8)
Therefore, the magnitude of the asymmetric broadening should be quite sensitive to the external field. At 70 Gc the shifts will be a factor of 2 smaller than at 35 Gc. To check this hypothesis the experiments on CsMnF$_3$ were repeated at 24 Gc. (This was simply accomplished by artificially enlarging the 30 Gc resonance cavity to 24 Gc with a high dielectric piece of sapphire, and running the 26.5 → 40 Gc spectrometer very close to cutoff with a K-band klystron.) Unfortunately, this experiment did nothing to clarify the situation. Briefly, the results were the following: On cooling the sample from room temperature to the transition region the line widths of both modes behaved qualitatively in the same manner as the corresponding line widths at 30 Gc, although the results were not quantitatively reproducible for different experimental runs. However, if the crystal was first cooled below $T_N$ before making these runs, the behavior was entirely different. Although there was still a tendency of the line widths to broaden near $T_N$, they were much narrower, showed larger asymmetries, and in general bore little resemblance to the earlier results. Furthermore, in the high frequency mode this new behavior abruptly disappeared below about 51°K and was replaced by a very broad resonance similar to the one observed at this temperature when the sample had not initially been cooled below $T_N$. This latter effect was also strongly field dependent, with a higher field inducing an earlier disappearance. Therefore, it seems likely that some sort of first-order, field dependent, phase transition takes place near $T_N$. In view of the complex structure of CsMnF$_3$, this result is not too surprising, although the radical change in the resonance behavior with only a 20% reduction in field and frequency was unexpected.
We therefore conclude that CsMnF$_3$ is much more complicated than anticipated, and until the reasons for the high sensitivity of its resonance properties to field and frequency are better understood, it is very difficult to make further attempts to understand the details of the line width behavior in the critical region.

In spite of the results at 24 Gc, it is interesting to consider possible reasons for the line width hump of the low frequency mode observed at 30 Gc. The existence of this second broad peak is surprising since such an effect has not been observed in MnF$_2$ or CsMnCl$_2$. This suggests that the peak may be due to sample dependent rather than intrinsic causes. Pursuing this possibility, we notice that the initial broadening of the peak strongly resembles the corresponding behavior of the sublattice magnetization in the same temperature region. Then if we postulate a distribution in the Neel temperature over the sample and assume that the AFR frequency expression contains a term dependent on long-range order (as predicted by the asymmetric broadening of the resonance absorption in the paramagnetic region), we can roughly explain the presence of the hump. That is, although we expect the intrinsic line width to narrow as the temperature is lowered below $T_N$, the distribution in Neel temperatures causes an inhomogeneous spread in resonance frequencies (because of the dependence of frequency on long-range order, which now varies over the sample), so that there is an overall broadening of the resonance line when this inhomogeneous effect exceeds the intrinsic line width. Furthermore, since the narrowest contributions to the line width will dominate, the resonance will broaden asymmetrically to low field, as observed experimentally. Since the amount of inhomogeneity depends directly on the variation of the local sublattice magnetization over the sample (and therefore on dM/dT), this
effect will peak and then gradually disappear as the temperature is lowered because of the nature of the Brillouin function. In particular, if we assume a $1 \rightarrow 2^0 K$ smear in $T_N$, then this explanation gives reasonably accurate predictions for the experimentally observed line width and resonance field behavior below $T_N$ of the low frequency mode at 30 Ge. Furthermore, such an effect would also contribute greatly to the line width behavior above $T_N$, and might account for some of the kinks.

Although this explanation makes qualitatively the correct predictions, it is difficult to imagine what mechanisms could produce such a large smear in the transition temperature of CsMnF$_3$. Spreads in $T_N$ of the order of degrees have been reported for other crystals, but only ones where the magnetic ion has a strong crystal field interaction. This is not the case in CsMnF$_3$ since the manganese ion is in an $S$-state. Also, the special characteristics of the low frequency absorption, such as the identical height of both peaks and the abrupt behavior at $T = 51.85^0 K$, is not really consistent with the idea of a smooth spread in $T_N$. Identical peak heights and abrupt behavior were also observed in crystal II, so it is more than coincidence. Therefore, although we do not have an alternative explanation at this time, we do not rule out the possibility that the Néel temperature may be well defined and that the unusual resonance behavior is due to intrinsic spin processes. In any case, the properties of CsMnF$_3$ are very complex in the critical region, and therefore, this crystal is less than ideal for a fundamental study of critical fluctuations.

C. Magnetic Anisotropy

Despite the complicated behavior of CsMnF$_3$ near the critical point, it is useful to consider its resonance properties in other temperature
regions where critical effects are not important. We have carried out such experiments over the entire paramagnetic temperature range below $300^\circ$K. Above approximately $75^\circ$K the asymmetric broadening associated with the critical region is negligible, so that these measurements provide a sensitive way of observing small resonance shifts that might occur in the paramagnetic region. In particular, we expect that the magnetic polarization of CsMnF$_3$ due to the applied field will produce anisotropies that will shift the resonance frequencies. Since the magnetic susceptibility, and hence the polarization, is temperature dependent, these shifts will also vary with temperature. Therefore, resonance experiments in the paramagnetic region provide a high temperature method for studying magnetic anisotropy, that is a useful supplement to the usual low temperature methods. The results of this experiment for two crystal orientations are shown in Fig. 8a for the temperature range $75 \rightarrow 150^\circ$K. In order to eliminate demagnetizing effects, these measurements were made on the spherical sample, crystal II.

To understand the difference in resonance frequencies for the two crystal orientations we must consider the microscopic reasons for anisotropy in CsMnF$_3$. Lee et al.\textsuperscript{16} have studied this problem at low temperatures, and showed that the experimentally observed negative axial anisotropy field could be roughly attributed to the magnetic dipolar and crystal field interactions. Furthermore, since Mn$^{++}$ is an S-state ion, the crystal field interaction is expected to be small, so that the predominant source of magnetic anisotropy can be attributed to the dipolar interaction. A very interesting feature of the dipolar anisotropy in CsMnF$_3$ is that it is due almost entirely to an intersublattice
interaction. This result can be understood qualitatively if we use the fact that the undistorted hexagonal structure can be obtained by two interlaced face-centered cubic (fcc) lattices, whose (111) planes correspond to the transverse planes of the hexagonal structure. Then in the two-sublattice approximation for CsMnF$_3$, each sublattice is represented by one of the fcc lattices. Therefore, since classical dipolar interactions cannot produce cubic anisotropy, the anisotropy is entirely due to interactions between sublattices, and as a result, the sign of the anisotropy depends on the relative directions of the sublattice magnetizations. Since the anisotropy is negative in the antiferromagnetic region (i.e., the basal plane is easy), we expect it to be positive in the paramagnetic region. That is, we expect a paramagnetic polarization of the spin system to have a preferred direction along the c-axis. Therefore, in a resonance experiment with c||H$_0$, the precessing spins see an additional field H$_a$ in the same direction as the applied field, where the magnitude of H$_a$ is proportional to the magnitude of H$_0$. The condition for resonance can then be written

$$\left(\omega/\gamma\right) \approx \left(H_0 + H_a\right)$$

so that the required resonance field is smaller because of the presence of anisotropy. The resonance condition is slightly more complicated with c||H$_0$. This is because the anisotropy energy is insensitive to spin precession in the plane (i.e., there is no in-plane anisotropy), so that the anisotropy field exerts a torque during only one half of the precessional cycle. The resonance frequency is then given by the
average

\[ \frac{\omega}{\gamma} \approx \left[ (H_o - H_a)(H_o) \right]^{1/2} \approx H_o - \frac{1}{2} H_a \quad cH_o \]  \hspace{2cm} (10)

where we have used the fact that \( H_a \) is opposite in direction to \( H_o \) when \( H_o \) is in the plane. Therefore, the splitting of the two resonances in the paramagnetic region should be \( (3/2)H_a \), and the shift with temperature of the resonance with \( cH_o \) should be twice the corresponding shift with \( cH_o \). Qualitatively, this is the behavior shown in Fig. 8a.

The temperature dependence of the splitting is determined by the corresponding behavior of the magnetic susceptibility. This is a result of the molecular field approximation, valid at high temperatures, that predicts the anisotropy field is proportional to the spin polarization. We can then write

\[ \frac{H_a(T)}{H_a(0)} \approx \chi(T)H_o/M(0) \quad T \gg T_N \]  \hspace{2cm} (11)

where \( H_a(0) \) and \( M(0) \) are the values of \( H_a \) and the total magnetization when the spins are all parallel, and \( \chi(T) \) is the susceptibility. Since \( \chi \approx C/(T + \theta) \), the splitting should increase as the temperature is lowered, which is again in qualitative agreement with experiment.

In order to make a quantitative comparison of theory with experiment it is necessary to consider the crystal field contribution. Lee et al.\textsuperscript{16} have estimated that the distortions of the fluorine octahedra surrounding the manganese sites produce a negative axial anisotropy field of magnitude \( H_{ac}(0) \approx 1000 \text{ Oe} \). Although this field will decrease in magnitude as the temperature is raised, it will not reverse sign in
the paramagnetic region like the corresponding dipolar anisotropy field. Then the effective anisotropy field in the antiferromagnetic region is the sum of $H_{ad}$ and $H_{ac}$ ($H_{ad}$ is the dipolar contribution), while in the paramagnetic region it is their difference. Low temperature torsion experiments have established $H_a \approx 7500$ Oe at $T = 0$, so that $H_{ad}(0) \approx 6500$ Oe. It is of interest to compare this result with the value predicted for $H_{ad}(0)$ by the room temperature experiments. From Eq. (11) we have $H_a(0) \approx 5250$ Oe, where we have used the experimental result that $H_a(300^\circ K) \approx 18$ Oe in an applied field $H_0 = 10,500$ Oe ($X(300^\circ K) = 10.6 \times 10^{-3}$ emu/mole and $M(0) = 27,700$ emu/mole in CsMnF$_3$). Since $H_a(0) = H_{ad}(0) - H_{ac}(0)$ in the paramagnetic region, we find $H_{ad}(0) \approx 6250$ Oe, which is in excellent agreement with the low temperature result. However, a theoretical calculation of $H_{ad}(0)$ based on the published structure of CsMnF$_3$ does not agree with these experimental results. With the aid of a computer, the dipolar anisotropy field was determined for both manganese sites by summing over all dipoles out to tenth nearest neighbors (convergence was quite rapid, with only 1% change occurring after the third nearest neighbors). Although these calculations verified the assumption that there is essentially no intra-sublattice contribution to the anisotropy, we found $H_{ad}(0) \approx 2700$ Oe. Assuming that this calculation is correct, it is difficult to understand why the experimentally observed values for the anisotropy are so much larger. For instance, it does no good to change the assumed value of the crystal field anisotropy because its value adds to $H_{ad}$ in the low temperature region, but subtracts from it in the paramagnetic region. What is needed is an additional source of anisotropy, such as a pseudodipolar interaction, that will behave like the dipolar anisotropy.
However, the presence of a pseudodipolar interaction depends on the spin-orbit coupling in the magnetic ions, and therefore its magnitude can be related to the deviation of the $g$-factor from 2. In S-state ions such as Mn$^{++}$, this deviation is very small, so that such interactions are usually neglected. Consequently, we have no explanation for this inconsistency between theory and experiment.

The observed temperature dependence of $H_a(T)$ is also in poor agreement with theory. This is illustrated by Fig. 8b, where the lower curve represents the temperature dependence of $H_a(T)$ as predicted by Eq. (11) and the assumption that $X = C/(T + \theta)$, with $\theta = 55^\circ$K. (This value of $\theta$ gives the best agreement with the measured values of $X$ for CsMnF$_3$ at $77^\circ$K and $300^\circ$K.) Since Eq. (11) was based on the molecular field approximation, it is not surprising that agreement with experiment becomes poorer as short-range order becomes more important near the transition temperature. However, we would expect the presence of short-range antiferromagnetic order to reduce the effective anisotropy field in the paramagnetic region, because of the opposite signs of the dipolar anisotropy above and below $T_N$. Instead, what is observed is a very definite increase in $H_a(T)$ with increasing short-range order. We have briefly considered the possibility that the shape of the clusters or the rate of convergence of the dipole sums might cause the initial contribution of short-range order to produce such an effect. This hypothesis was checked by introducing an anisotropic correlation length into our previous computer calculations for the dipolar anisotropy field, but the results were negative. Therefore, at the present time we do not quantitatively understand either the magnitude or the temperature dependence of the resonance effects of magnetic anisotropy at high temperatures.
V. RELAXATION IN CUBIC ANTIFERROMAGNETS; $T \geq T_N$

A. Introduction

In the last section we saw that the experimentally observed resonance line widths in CsMnF$_3$ in the critical region were probably not due to intrinsic spin relaxation. Instead, asymmetric broadenings predominated and were tentatively attributed to the combined effects of the large anisotropy field, a smear in the Neél temperature, and further complications related to the complex structural and magnetic properties of this crystal. It is therefore of interest to consider the opposite extreme, i.e., the low anisotropy cubic antiferromagnets RbMnF$_3$ and KMnF$_3$. Since these crystals above $T_N$ are excellent approximations to the ideal Heisenberg antiferromagnet and their Neél temperatures are well defined, then the paramagnetic resonance line widths should be directly related to the time and spatial correlation of the electronic spin arrangement at all temperatures. Therefore, experiments on these crystals offer an excellent opportunity to check the conventional theories of critical fluctuations and spin relaxation. In this section we present the results of such experiments, compare them with the predictions of the conventional theory, and then suggest possible modifications to this theory that will help to resolve the inconsistencies between theory and experiment.

B. Experimental Results

The line width behavior of RbMnF$_3$ in the paramagnetic temperature region is shown in Fig. 9a. Variations in line width and g-value amounted to less than 1% as the sample temperature was varied continuously from room temperature to just below the transition temperature. In the immediate vicinity of $T_N$, line width measurements were made less
than .01 K apart with no indication of anomalous behavior. The experiment was repeated for other crystal orientations with no qualitative change in results.

Similar experiments were carried out on KMnF$_3$ by both this author and Dr. G. Witt. The line width behavior just below and in the immediate vicinity of $T_N$ is complicated by an AFR splitting of the main resonance line, associated with the twinned nature of this crystal below 184 K. However, as in RbMnF$_3$, there appears to be a negligible variation in the intrinsic line width as the temperature is lowered from room temperature through $T_N$. These results are shown in Fig. 9b.

It is worth noting that similar measurements have been made on the cubic antiferromagnet KMnCl$_3$ by Kedzie et al. where, again, no detectable temperature dependence of the paramagnetic resonance line width was observed. In this experiment, however, measurements were made at relatively large temperature intervals (1 → 2 K) so that the possibility of an anomalous line width increase in a narrow interval near $T_N$ was not completely ruled out.

There are no simple explanations for this rather negative behavior of cubic antiferromagnets in the critical region. As mentioned in the introduction, we would expect the line width to directly reflect the considerable spin correlation known to exist in the vicinity of the critical point. The lack of an anomalous behavior suggests that the problem is somewhat more complicated than expected. We will, therefore, devote considerable space in the following section to a detailed discussion of the theory of line widths before making comparisons with experiment.
C. Conventional Theory of Line Widths

Introduction

Most theoretical expressions for the resonance line width in magnetic materials involve simplifying assumptions that restrict their range of application to narrow intervals of temperature. For instance, Dyson's theory of spin wave interactions and damping, which is valid in the low temperature limit, appears unrelated to the corresponding line width expression for resonance in the high temperature, exchange narrowed region.

In view of this, it is often difficult to interpret resonance data taken in the intermediate temperature range near a magnetic transition, since we would expect both the collective effects characteristic of low temperatures and the rapid spin modulation effects characteristic of high temperatures to be present simultaneously.

What is usually done in analyzing the intermediate range is to generalize the corresponding temperature limited expression to finite temperatures. For example, in interpreting the paramagnetic resonance line width of nickel near the transition temperature, Salamon attempted to generalize the Anderson and Weiss high temperature theory of exchange narrowing to the transition temperature region. This approach is attractive because, in view of the simple model on which the Anderson and Weiss theory is based, the results of the generalized model can also be easily interpreted physically. However, it seems such a generalization is rigorously possible only in the simplest resonance systems. In more complicated systems the generalization procedure relies heavily on "physical intuition" and therefore the results are often suspect.

What is really needed is a single line width expression valid for all temperatures; then any approximations made in applying it to a given
temperature region can be justified rigorously. Mori and Kawasaki have derived such an expression for the damping of the spin components in ferro- and antiferro-magnets. A straightforward reduction of their expression in the low temperature limit leads to a description of spin wave damping consistent with that of Dyson, and in the high temperature limit it reduces to the familiar exchange narrowed linewidth formula. Therefore, it is ideal for a discussion of damping in the critical region and will be used as the basis of our analysis. In the next section the Mori and Kawasaki theory will be introduced and then applied to a simple example of interest. This section is followed by a general discussion of the conventional theory of critical fluctuations. Finally, in the last section the results are combined to give theoretical predictions for the linewidth behavior of cubic isotropic crystals in the critical region.

**Mori-Kawasaki Formulation**

A theory of many particle systems has been developed by Mori and Kawasaki to formulate transport, collective motion, and Brownian motion from a unified, statistical-mechanical point of view. Their derivation is discussed briefly in Appendix I, where it is shown that in the special case of a spin system with axial symmetry about the direction of the applied field the expression for the paramagnetic resonance linewidth reduces to $\Delta H = \Gamma_0^{\pm}/\gamma$, where $\Gamma_0^{\pm}$ is the damping constant of the total transverse magnetization $M^{\pm}$ and is given by

$$\Gamma_0^{\pm} = \text{Re} \int_0^\infty dt e^{-i\Omega_o t} \langle \{f^+(t), f^-\} \rangle \langle \{M^+, M^-\} \rangle$$

where $\Omega_o$ is the Zeeman frequency $\gamma H$, and $f^\pm(t)$ is a random torque defined
at $t = 0$ by $f^\pm = \dot{M}^\pm + i\Omega_o M^\pm$. ($\dot{M}$ is the time derivative of $M^\pm$ and is determined in the Heisenberg manner by taking the commutator of $M^\pm$ with the system Hamiltonian.) In deriving this equation we have assumed our system satisfies the extreme narrowing condition $\Gamma_o^+ \tau_c \ll 1$, where $\tau_c$ is the correlation time of $f^+(t)$, so that the central portion of the resonance line is Lorentzian. We have also ignored the possibility of intrinsic collective oscillations above the transition temperature, so that the magnetization is diffusion like in its decay and dies away exponentially with time.

In order to gain a physical understanding of the form of this damping expression, it is useful to consider the simple example of spin relaxation due to the dipolar interaction in magnetic crystals in the high temperature limit. If we also assume there is no anisotropy, then the system Hamiltonian is written as

$$
H = \gamma nE I S^Z - \sum_{i,j} J_{ij} S_i \cdot S_j + \sum_{i,j} K_{ij} (3S_i^Z S_j^Z - S_i \cdot S_j) ,
$$

where the terms on the right are the Zeeman, exchange, and dipolar terms, respectively (the prime on the summation indicates $i \neq j$). For simplicity we have neglected the nonsecular dipolar terms so that

$$
K_{ij} = (\frac{\gamma^2 n^2}{4})(1 - 3 \cos^2 \theta_{ij})/R_{ij}^3 ,
$$

where $\theta_{ij}$ is the polar angle of $R_{ij}$, the vector between spins $i$ and $j$. We then find

$$
\dot{I}^\pm = \pm i\gamma \sum_{i,j} K_{ij} S_i^Z S_j^\mp ,
$$
and therefore, the expression for the damping involves rather complicated four-spin, time correlation functions. In order to evaluate the damping constant it is necessary to perform the exact integration of these time correlation functions. However, this is usually prohibitively difficult unless we know their decay form. Anderson and Weiss have shown in the high temperature limit that it is an excellent approximation to assume the Gaussian decay

$$\langle (\hat{r}^+, t), \hat{r}^- \rangle = \langle (\hat{r}^+, \hat{r}^-) \rangle e^{i \nu t} e^{-t^2/\tau_c^2}, \quad (16)$$

where $\nu$ and $\tau_c$ are rigorously given by the first and second moments of this correlation function, i.e.,

$$i\nu = \langle (\hat{r}^+, \hat{r}^-) \rangle / \langle (\hat{r}^+, \hat{r}^-) \rangle, \quad \frac{1}{\tau_c^2} = -\nu^2 + \langle (\hat{r}^+, \hat{r}^-) \rangle / \langle (\hat{r}^+, \hat{r}^-) \rangle. \quad (17)$$

In the critical region, however, there is no reason to expect this is still a good approximation. Therefore, for the moment, we will avoid this problem by defining $\tau_c$ quite generally as

$$\tau_c = \Re \int_0^\infty dt \ e^{-i \Omega t} \langle \hat{r}^+(t), \hat{r}^- \rangle / \langle (\hat{r}^+, \hat{r}^-) \rangle. \quad (18)$$

Combining these results, we can then express the damping at a general temperature above the critical point as
\[ \Gamma_0^+ \approx \frac{(36)}{d^2} \tau_c \frac{\Sigma'_{\alpha\beta} \Sigma'_{\mu\nu} K_{\alpha\mu} K_{\beta\nu} \langle (s'^{\alpha}_{\alpha} s'^{\beta}_{\beta} s'^{\mu}_{\mu} s'^{\nu}_{\nu}) \rangle}{\Sigma_{\alpha\beta} \langle (s'^{\alpha}_{\alpha} s'^{\beta}_{\beta}) \rangle} \]  \hspace{1cm} (19)

In the high temperature limit, a rigorous evaluation\textsuperscript{27} of Eq. (17) (assuming a Gaussian decay) yields the expected result that \( \tau_c^{-1} \approx \omega_e \), where \( \omega_e \), the exchange frequency, is proportional to the exchange coupling expressed in frequency units. Also, at high temperatures, there is essentially no spin correlation, i.e.,

\[ \langle (s'^{\alpha}_{\alpha} s'^{\beta}_{\beta}) \rangle = \frac{1}{3} S(S+1) \delta_{\alpha\beta} \delta_{\alpha' \beta'} \] \hspace{1cm} (20)

where \( \alpha \) and \( \beta \) denote the different spin components. Then in this special case, Eq. (19) reduces to

\[ \Gamma_0^+ = A \gamma^4 \hbar S(S+1) \omega_e^{-1} \Sigma'_{\alpha\beta} (1 - 3 \cos^2 \theta_{\alpha \beta})^2 \tau_{ij}^6 \equiv \omega_D / \omega_e \] \hspace{1cm} (21)

where \( A \) is a numerical constant. This is just the Anderson and Weiss expression for exchange narrowing. For a simple cubic lattice, where for simplicity we perform an average over all crystal orientations, it can be shown\textsuperscript{25}

\[ \omega_D^2 = 5.1 \gamma^4 \hbar S(S+1) / d^6 \] \hspace{1cm} (22)

\[ \omega_e^2 = 2.8 J^2 S(S+1) \] ,

where \( d \) is the lattice constant and \( J \) is the exchange integral. Using
the values for $\omega_e$ and $d$ given in Sec. III and the relation $\Delta H = \Gamma \sqrt{1/\gamma}$, we find $\Delta H \approx 20$ Oe in $\text{KMnF}_3$ and $\Delta H \approx 30$ Oe in $\text{RbMnF}_3$. Since in the above derivation we neglected the non-secular contributions to the line width, we must multiply these results by $10/3$, and obtain $\Delta H \approx 75 \pm 15$ Oe. This is in excellent agreement with the observed value $\Delta H \approx 60$ Oe in both crystals, and clearly demonstrates the validity of the Anderson and Weiss model at high temperatures.

This simple example gives a good illustration of the two major approximations in the Anderson and Weiss model: 1. The sole effect of exchange is to randomly modulate the dipolar field at the exchange frequency, thus time-averaging the broadening mechanism; 2. There is no spin correlation. Conventional theory, however, predicts anomalous increases in the time and spatial correlation of the electronic spin arrangement in the critical region. Therefore, the simple result of Eq. (21) is no longer valid, and we must return to the general damping expression, Eq. (19), involving four-spin correlation functions and the temperature dependent parameter $\tau_c$, in order to rigorously determine the effect of increased correlation on line widths. However, in practice it is virtually impossible to predict the behavior of the damping constant in the critical region from this expression unless simplifying approximations are made. Usually these approximations are ones relating the critical behavior of $\tau_c$ and the four-spin correlation functions to the more familiar behavior, both experimentally and theoretically, of the two-spin, time dependent correlation function $P^{\alpha\beta}(S_i^t, t) = \langle S_i^t(t), S_j^\beta \rangle$. Therefore, before proceeding to this problem of simplification, we will briefly review the conventional theory of critical fluctuations and its predicted behavior for the pair correlation function.
Conventional Theory of Critical Fluctuations

As the transition temperature is approached from above, correlation in the electronic spin system increases, both in space and time. Roughly speaking, we can picture the spin arrangement at any instant of time as consisting of clusters of ordered spins. These clusters are constantly dissolving and reforming, since in the paramagnetic region the time average value of the spin at any site is zero. The fluctuations in cluster size and lifetime increase enormously near the critical temperature and are called magnetic critical fluctuations.

The physical reason for these large fluctuations is that the minimum work necessary to produce them goes to zero as the critical point is approached. In magnetic systems this minimum energy necessary for a given spontaneous fluctuation can be related to a wave number-dependent tensor susceptibility, \( \chi^{\alpha \beta}(q) \), which gives the magnetic moment response in the \( \alpha \)-direction to a steady sinusoidal magnetic field, with wave vector \( k \), in the \( \beta \)-direction. There are several approaches used to calculate \( \chi^{\alpha \beta}(q) \) in the transition region, all of them approximations. The Ornstein-Zernike theory of critical scattering as adapted by Van Hove for neutron scattering makes the prediction for the diagonal components

\[
\chi^{\alpha \alpha}(q) = \chi^{\alpha \alpha}(q) + q = \chi_0 \left( \frac{\chi_0}{\chi^{\alpha \alpha}(q)} + r_2^2 q^2 \right) \quad (q \to 0, T \to T_c) \quad (23)
\]

where \( q \) is just the deviation of \( k \) from a magnetic reciprocal lattice vector \( K_0 \), \( \chi^{\alpha \alpha}(q_0) \) is the corresponding staggered susceptibility, \( \chi_0 \) is the Curie susceptibility in the absence of exchange, and \( r_2 \) is a temperature insensitive microscopic length defined by Van Hove. Recent
neutron experiments on metallic iron\textsuperscript{30} and KMnF\textsubscript{3}\textsuperscript{31} have confirmed that the general form of Eq. (23) is correct within experimental error.

Moriya\textsuperscript{2} obtained an explicit relation between the susceptibility tensor and the size of the corresponding fluctuations by first defining the Fourier transform spin deviations

\[ S^\alpha_R(t) = N^{-\frac{1}{2}} \sum_j S^\alpha_j(t) e^{i\mathbf{k} \cdot \mathbf{R}_j} \quad (24) \]

where \( N \) is the number of magnetic ions in the crystal. We can then rewrite the time dependent, pair correlation function as

\[ \rho^{AB}(\mathbf{R}_k, t) = N^{-1} \sum_k \langle (S^\alpha_k(t), S^\beta_k(0)) \rangle e^{-i\mathbf{k} \cdot \mathbf{R}_k} \quad (25) \]

There correlation function \( \langle (S^\alpha_k(t), S^\beta_k(0)) \rangle \) describes the size and lifetime of the \( k \)-th spontaneous fluctuation. The static part of this correlation function, which characterizes the probability the fluctuation will occur, is directly related to the susceptibility tensor by the fluctuation-dissipation theorem,\textsuperscript{32} i.e.,

\[ \langle (S^\alpha_k(0), S^\beta_k(0)) \rangle = \delta_{\alpha\beta} \frac{k_B T}{\gamma n^2} \chi^{AB}(k) \quad (26) \]

where we have assumed the dominate interaction is an isotropic exchange interaction so that only the terms with \( \alpha \) and \( \beta \) equal contribute. This relation tells us that in ferromagnets the most probably fluctuations occur in the local magnetization. In antiferromagnets, however, it is the staggered susceptibility that becomes anomalously large near \( T_N \).
and therefore the dominate fluctuations give rise to clusters of anti-
ferromagnetically aligned spins.

If we use the Ornstein-Zernike form for $X(k)$ and take the Fourier
transform of Eq. (26), we have the familiar screened-Coulomb-potential-
like expression for the pair correlation function

$$
\langle [s_{i}^\alpha(0), s_{j}^\beta(0)^{\ast}] \rangle = \pm \delta_{\alpha\beta} \left( \frac{V}{N} \right) \frac{s(s+1)}{2} \frac{1}{4\pi r_{ij}^2} \frac{e^{-kr_{ij}}}{r_{ij}}, \quad \text{or} \quad r_{ij} \to \infty,
$$

where the sign is determined by whether or not $s_{i}$ and $s_{j}$ are on the same
sublattice. $\kappa$ is the inverse of the pair correlation distance, and is
defined by

$$
(\kappa r_{ij}) = \frac{x_{0}}{x(k_{0})}.
$$

Therefore, in the critical region, the pair correlation length diverges
as the square root of the staggered susceptibility. Recent investigation,
both experimental$^{30}$ and theoretical$^{33}$ suggest a $4/3$ power law for the
divergence of the staggered susceptibility in Heisenberg spin systems
with a cubic structure.

Calculation of the time dependence of the pair-correlation functions
is considerably more complicated. Moriya$^{2}$ employed the technique developed
by Mori and Kawasaki that is discussed in Appendix I. Applying their
result (Eq.(A.10) of the Appendix) to the normal mode Fourier spin com-
ponents ($\alpha, \beta = z, \pm$), we have

$$
\langle [s_{i}^\alpha(t), s_{j}^\beta(t)] \rangle = \langle [s_{i}^\alpha, s_{j}^\beta^{*}] \rangle e^{(i\hbar_{k} - r_{ij}^{\alpha})t} ; \quad (t \gg \tau_{k}),
$$

(29a)
where

$$\Gamma_k^\alpha = \text{Re}(\Gamma_k^\alpha) = \text{Re} \int_0^\infty dt e^{-i\Omega_k t} \left\langle \left\{ r_k^\alpha(t), r_k^\alpha* \right\} \right\rangle / \left\langle \left\{ r_k^\alpha, r_k^\alpha* \right\} \right\rangle ;$$

\[ (\Gamma_k^\alpha \tau_k \ll 1) . \]  

(29b)

The exponential time decay of Eq. (29a) means we have again assumed the power spectrum of $S_k^\alpha$ is of the cutoff Lorentz form, and therefore $\Gamma_k^\alpha$ is just the half-width at half-height. Conventional theory further assumes the absence of collective oscillations above the transition temperature so that $\Omega_k = 0$, which says the fluctuations do not propagate and are consequently diffusion-like in their decay. This is a major assumption of the conventional approach that will later prove to be suspect.

As before, a rigorous evaluation of the integral in Eq. (29b) is prohibitively difficult except at high temperature. We can write this expression in a more convenient form by defining the correlation time $\tau_k^\alpha$ of the $k$-th component of the torque, in analogy with Eq. (18). Then with the aid of Eq. (26), we can write

$$\Gamma_k^\alpha = \Gamma_k^\alpha + q = \frac{1}{N} \frac{3\chi_0}{s(s+1)y^2 n^2} \frac{\tau_{K_0} + q}{\chi_{K_0}^q + q} \left\langle \left\{ r_{K_0}^\alpha + q, r_{K_0}^\alpha * + q \right\} \right\rangle$$

(30)

With exchange as the only interaction and in the high temperature limit, the static correlation function in this expression reduces for small $q$ to a term dependent on $q^2$ in ferromagnets, and to a constant in antiferromagnets.\(^2\) This additional quadratic dependence of $\Gamma_k^\alpha$ on $q$ in a ferromagnet is a purely kinematic effect\(^3\) which stems from the fact $S_{K_0}$ is a constant of the motion in a ferromagnet, but not in an antiferromagnet. Therefore, we expect
this effect to be present at all temperatures, and write

\[ \Gamma_{K_0+q}^{K_0+q} \approx \frac{L(K_0+q)}{X(K_0+q)} q^2 \equiv \Lambda(K_0+q) q^2 \quad (q \to 0, T \to T_c) \]  

(31a)

for a ferromagnet, and

\[ \Gamma_{K_0+q}^{K_0+q} \approx \frac{L(K_0+q)}{X(K_0+q)} \equiv \Lambda(K_0+q) \quad (q \to 0, T \to T_N) \]  

(31b)

for an antiferromagnet, where \( L(K_0+q) \) corresponds to the Onsager kinetic coefficient of irreversible thermodynamics and \( \Lambda(K_0+q) \) is a generalized \( q \)-dependent diffusion constant. In analogy with molecular diffusion in critical mixtures of liquids,\(^{35}\) it is usually assumed \( L(K_0+q) \) is slowly varying with temperature in the critical region. This will turn out to be a questionable approximation in spin systems, and will be discussed in detail in a later section. The inverse dependence of \( \Gamma_k \) on \( X(k) \) describes the "thermodynamic slowing-down" characteristic of both ferro- and antiferromagnets. Heller has given this dependence physical significance by pointing out that the decay of a fluctuation is inhibited by the molecular field generated by that fluctuation. Since by definition \( X(k) \) describes the system response to such a molecular field, an inverse dependence of the decay rate on \( X(k) \) is to be expected. In particular, this effect leads to a particularly slow decay near \( T_N \) of fluctuations close to a reciprocal lattice vector, since we know at the transition temperature the \( k = K_0 \) fluctuation becomes self-sustaining, i.e., \( X(K_0) \to \infty \) as \( T \to T_N \).

Relaxation Times

We now return to our earlier example of dipolar spin relaxation in a
cubic crystal with no anisotropy, where we found for a general temperature in the paramagnetic region

$$\Gamma_0^\pm \approx \frac{1}{N} \frac{16\beta}{S(N+1)k_B^2} \left( \frac{X}{\chi} \right)^{1/2} \sum_{i,j,k,m} K_{ij} K_{km} \langle [S_i^z S_j^z, S_k^z S_m^z] \rangle$$

where \(X\) is the static susceptibility and we have used Eqs. (24) and (26) to write Eq. (19) in this form. The inverse dependence of \(\Gamma_0^\pm\) on \(X\) is just another manifestation of the thermodynamic slowing-down in the critical region described in the previous section. It predicts a large narrowing of the paramagnetic resonance line width in ferromagnets as \(T \to T_C\), while in antiferromagnets it predicts a slight broadening. However, this effect is of secondary interest to the critical behavior of the other temperature dependent factors in this expression, which we will now examine.

In order to determine the temperature dependence of the four-spin correlation functions due to increased spatial correlation in the critical region, it is necessary to approximate them by the product of pair correlation functions of four spin operators. This is a good approximation if we work fairly apart from the critical region, i.e., in the temperature region where \(Z\) is the number of neighboring spins (usually \(Z \sim 10\)). Since the Ornstein-Zernike formula for pair correlation is also restricted by this condition, we might expect the anomalies are large enough even in this region to discuss their principal mechanisms. Therefore, we write

$$\langle [S_i^z S_j^z, S_k^z S_m^z] \rangle \approx \langle S_i^z \rangle \langle S_k^z \rangle \langle S_j^z \rangle \langle S_m^z \rangle$$
where we have assumed that three-spin correlation functions vanish above the critical temperature, as well as other pair products such as \( \langle S_i^Z S_j^+ \rangle \), etc. In a cubic system without anisotropy the fluctuations are isotropic, i.e., \( \langle S_i^Z S_j^Z \rangle = 1/2 \langle [S_i^+, S_j^-] \rangle \). Then the static correlation function of Eq. (32) can be written

\[
\langle [x^+, x^-] \rangle \approx 36\gamma^2 \sum_{i,j} K_{ij} K_{km} \langle S_i^Z S_k^Z \rangle \langle S_j^Z S_m^Z \rangle
\]  

(35)

This expression will exhibit anomalous behavior in the critical region only if it includes terms with long range correlation between spins. (The static correlation function of spins situated very close to each other varies slowly with temperature near \( T_N \) and, hence its temperature dependence can be ignored in the first approximation.\(^6\)) In cubic crystals all such long range terms vanish, as can be seen from the following argument: We are interested only in correlation between spins \( S_1 \) and \( S_3 \) a large distance \( R_{1k} \) apart. Since \( K_{ij} \) falls off as \( R_{ij}^{-3} \), this suggests only terms with \( R_{jm} \) also large make significant contributions to the anomalous behavior of Eq. (35) (i.e., only terms where \( S_1 \) and \( S_j \), as well as \( S_k \) and \( S_m \), are reasonably close together are important). Then in this approximation \( (R_{jm} \) large), \( \langle S_j^Z S_m^Z \rangle \) is roughly independent of the index \( m \) for a given shell of neighbors to the spin \( S_k \). Then the long range terms of Eq. (35) can be written approximately as

\[
36\gamma^2 \sum_{i,j} K_{ij} K_{km} \langle S_i^Z S_k^Z \rangle \sum_s \langle S_j^Z S_m^Z \rangle \Sigma \langle S_i^Z S_s^Z \rangle K_{km} = 0
\]  

(36)

since \( \Sigma_m K_{km} = 0 \) in a cubic crystal. (\( s \) represents the \( s \)-th shell of nearest neighbors to \( S_k \), and \( m \) now represents spins within a shell.)
Therefore, in cubic crystals, spin damping is insensitive to spatial correlation (excluding the dependence on \(X_0/X\), and within the limits of the pair approximation) and any anomalous behavior of \(\Gamma_0^\pm\) is a direct consequence of anomalous behavior in the time correlation of the torque.

At present there is no satisfactory way of rigorously determining the temperature dependence of the correlation time of the torque. Only in the special case where we know the decay form of the random torque can a rigorous expression for \(\tau_c\) be derived. An example of this is the Gaussian decay, assumed valid in the high temperature limit, that we considered earlier. In this case we see from Eq. (17) that the temperature dependence of \(\tau_c\) is determined by the corresponding temperature dependence of two static correlation functions involving the torque and its derivative. However, in the critical region a Gaussian decay is no longer a good approximation.

Mori\(^7\) has considered this problem in detail and derived quite generally a continued-fraction representation for time correlation functions, which enabled him to express \(\tau_c\) as an infinite expansion of static, time independent correlation functions, i.e.,

\[
\Delta_1^2 \tau_c = \lim_{\varepsilon \to 0} \frac{\Delta_1^2}{\varepsilon + \Delta_2^2} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (37)
\]

where \(\Delta_j^2 = \langle \{f_j^+, f_j^-\} \rangle / \langle \{f_{j-1}^+, f_{j-1}^-\} \rangle\) and
Since this expression for $T_c$ was derived without making any particular assumption about the decay form of the random torque it is valid in the critical region. Mori then inferred that if none of the static correlation functions of this expansion showed anomalous behavior in the critical region, then $T_c$ would also show no anomalous behavior. In particular, if this approach is applied to the case considered above of dipolar broadening in cubic crystals, it predicts $T_c$ is at most slowly varying near $T_N$ (since all the correlation functions in the expansion can be shown to reduce to functions describing correlation between spins situated very close together). Therefore, from Eq. (32), the line width behavior in the critical region should be determined by the corresponding behavior of the static susceptibility, and hence, in antiferromagnets there should be at most a slight broadening of the resonance line in the transition temperature region.

Unfortunately, this continued-fraction approach and its predicted behavior for $T_c$ suffers from the fact that it involves the rather difficult problem of studying the singularity of a function from a finite number of terms of a series expansion, where the convergence of this expansion, especially near the critical point, remains unanswered. For this reason Kawaski recently questioned the results of this approach and suggested that under certain circumstances $T_c$ might well be very sensitive to temperature in the transition region. A strong temperature dependence of $T_c$ is to be expected if we use the "physical" interpretation of the Anderson
and Weiss\textsuperscript{24} model that $\tau_c^{-1}$ is the frequency at which the dipolar local field is randomly modulated by exchange, so that each precessing spin executes a random walk in phase angle with respect to the rotating frame of the total magnetization, with a time $\tau_c$ between each step. Using this intuitive definition, the following qualitative derivation of the temperature dependence of $\tau_c$ seems reasonable:\textsuperscript{26} The motion of a spin $S_1$ is predominately determined by its interaction with the exchange field

$$F_1 = -\Sigma_j J_{ij} S_j$$

due to the neighbors $S_j$. Since the number of $S_j$'s is large, the motion of $F_1$ is not rapid when compared with the motion of $S_1$; thus, a good approximation to the correlation time of any exchange modulated interaction between a spin and its neighbors should be approximately the mean oriented lifetime $\tau$ of a single spin. This lifetime is simply the average overall $k$-states of the probability that a spin will take part in the $k$-th fluctuation times the fluctuation lifetime.\textsuperscript{2} We then have

$$\tau_c \approx \tau = \frac{4\pi A}{\int_0^\infty (\Gamma_{K_0 + q})^{-1} \times (K_0 + q)^2 dq} (T \to T_c) \quad (38)$$

where $A$ is a constant. Using Eqs. (23) and (31) we have $\tau_c \propto (kr_1)^{-3}$ for ferromagnets and $\tau_c \propto (kr_1)^{-1}$ for antiferromagnets, where we have used the conventional theory assumption that $L(K_0 + q)$, the Onsager kinetic coefficient, is slowly varying in the critical region. Referring to Eq. (28), this result therefore predicts a rapid increase in the mean electronic lifetime, and, hence, in the line width (excluding the $X_0/X$ dependence), as the transition temperature is approached from above. Moriya has explicitly evaluated the proportionality constant in these two expressions for $\tau_c$ for several types of lattices, and found it to be of the order of
\(10^{-1} \tau_c\) in cubic antiferromagnets, where \(\tau_c\) is the correlation time in the high temperature limit. The broadening in antiferromagnets will consequently occur in the narrow temperature interval defined by \((kr_1)^{-1} \geq 10\) (e.g., if \(T_N \approx 100^\circ K\) then \((kr_1)^{-1} \geq 10\) if \(T - T_N \leq 1^\circ K\)).

We therefore have two contradictory predictions for the temperature dependence of \(\tau_c\), and it is still an open question which prediction is closer to the truth. The intuitive argument is a little weak since \(\tau_c\) is actually the correlation time of the torque acting on the total magnetization, not just on an individual spin, and consequently it is difficult to picture physically. On the other hand, Kawasaki has found weaknesses in the continued-fraction approach. Therefore, we will attempt to use the following comparison of theory with experiment as a means for deciding between these two possibilities. It will turn out that the predictions of the continued-fraction approach cannot be reconciled with the existing experimental data on ferro- and antiferro-magnets in the critical region, so that the intuitive argument, although requiring some fundamental modifications, is to be preferred.

D. Comparison with Experiment; Limitations of Conventional Theory

The experimental results on \(\text{RbMnF}_3\) and \(\text{KMnF}_3\) are completely inconsistent with the line width behavior predicted by the intuitive argument. The line width does not increase anomalously in either crystal, suggesting that perhaps the continued-fraction approach, which predicts the line width behavior is determined solely by the corresponding behavior of the static susceptibility, is the correct one. However, this prediction is inconsistent with the results of line width measurements made by Salamon.
on cubic, ferromagnetic nickel in the critical region. These results are shown in Fig. 10 where we see the predicted \( X_0/X \) dependence is valid only to about 385°C \((T_c + 30^\circ K)\), where an additional temperature dependence appears. \( (X \) has been replaced by \( M/H \) in the critical region. \( ^{39} \) Therefore, both theories in their present form are inconsistent with the existing experimental data and we must look for possible modifications. Since the only question of validity of the continued-fraction approach concerns mathematical problems of convergence, there are no obvious modifications and we must assume the data on nickel rules out the results of this approach. We therefore look for ways to modify the remaining intuitive derivation, that will resolve the inconsistencies between theory and experiment.

A clue to finding such a modification is provided by Salamon's interpretation of his measurements on nickel. After factoring the \( X_0/X \) dependence a sharp line width increase remains, which can be explained by assuming \( \tau_c \) diverges as \( \kappa^{-1} \) in the critical region. This is contrary to our prediction that \( \tau_c \propto \kappa^{-3} \) for ferromagnets. Salamon suggested this discrepancy could be resolved by assuming the diffusion constant remained constant, and approximately equal to its room temperature value, in the critical region (rather than going to zero as \( X^{-1} \), as predicted by conventional theory). This assumption, which at first sight appears equivalent to ignoring the thermodynamic slowing-down of fluctuations, seemed to be supported by inelastic neutron scattering experiments, \(^1\) which measure the fluctuation lifetimes directly. Then from Eqs. (38) and (31), we see that this implies the anomalous line width increase in nickel is due solely to the kinematic slowing-down characteristic of ferromagnets, and indeed,
$\tau_c$ does diverge as $\kappa^{-1}$ in this approximation. If the same assumption is made in antiferromagnets [i.e., $\Lambda(K_o+q) \neq f(T)$], then $\tau_c$ remains constant in the critical region as predicted by our experimental results. However, there are several problems with this assumption, a major one being its apparent inconsistency. For instance, the dominant line width behavior observed in nickel is a narrowing due to the $\chi/\chi_0$ dependence, which is just another manifestation of the thermodynamic slowing down. Yet, in calculating the temperature dependence of $\tau_c$, this same effect is ignored in order to explain the data.

Recently two independent, and quite different, explanations for this "inconsistent" behavior of the diffusion constant have been proposed. The first explanation, given by Marshall, suggests the possibility that spin-wave-like collective modes are present above the critical point, in addition to the critical fluctuations assumed by conventional theory. The existence of collective spin modes in the critical region will clearly modify our previous calculation for the effective frequency at which the dipolar interaction is randomly modulated by exchange. Another explanation, more recently proposed by Kawasaki, suggests the conventional theory of spin diffusion is not appropriate for Heisenberg spin systems for very fundamental reasons. In particular, the assumption that the Onsager kinetic coefficient is slowly varying in the critical region is questioned. Both of these modifications to the conventional theory are not inconsistent, so it is possible they are simultaneously present. In the following sections we will discuss these explanations in some detail, and then show how they improve our understanding of the critical behavior of line widths.
Kawasaki Proposal \(^{38}\)

In an effort to understand the apparent failure of the diffusion constant to vanish at the Curie point, Kawasaki re-examined the formal definition of the generalized diffusion constant given by Eq. (31), i.e.,

\[
\Lambda(K_0 + q) = L(K_0 + q)/\chi(K_0 + q).
\]

Then from this point of view, the possibility that the diffusion constant \(\Lambda(K_0)\) does not vanish at \(T_C\) implies that the Onsager kinetic coefficient \(L(K_0)\) must diverge at the Curie point, since the divergence of \(\chi(K_0)\) at \(T_C\) is a well established fact. To study this possibility we must first look at the behavior of \(L(K_0 + q)\) from a microscopic point of view. Using Eqs. (30) and (31) we can write

\[
\int_{s}^{\Lambda^{(3)}} = \frac{1}{N} \frac{3\chi_0}{S(S+1)\gamma^2 h^2} \tau_k \langle \hat{f}_{k}^{(X)} \hat{f}_{k'}^{(X)} \rangle \quad (39)
\]

where \(\tau_k^{(X)}(t)\) is the random torque due to the exchange interaction acting on the \(k\)-th magnetization fluctuation and \(\tau_k\) is the corresponding correlation time. The Mori continued-fraction representation predicts \(\tau_{K_0+q}\) [and therefore \(L(K_0 + q)\)] is slowly varying with temperature in the critical region, and we will now show that this is a questionable result for small \(q\). The torque can be expressed at \(t = 0\) as an expansion of the Fourier spin operators, \(^{27}\) i.e.,

\[
\tau_k^{(X)} = \frac{N^2}{N} \sum_{k} J(k, K_0 + q-k) \hat{s}_{k}^{+} \hat{s}_{k}^{-} \quad (40)
\]

where we arbitrarily choose \(\alpha = z\) in order to be explicit, and the particular form of the coefficients \(J(k,k')\) is not important for this qualitative discussion. The important point to realize here is that we have been able to expand the torque in terms of the macroscopic variables exhibiting
critical fluctuations, i.e., those particular \( S_k \) with \( k \) close to \( K_0 \).

Therefore, we should be able to check the consistency of the conventional theory by using the generalized diffusion equation

\[
\frac{\partial}{\partial t} S_{K_0+q} = -\Gamma_{K_0+q} S_{K_0+q} \quad (q \to 0, T \to T_c) \tag{41}
\]

to describe the time dependence of these macroscopic variables in evaluating the time correlation function expression for \( L(K_0+q) \). Since the decay rates \( \Gamma_{K_0+q} \) are directly related to the corresponding \( L(K_0+q) \) [by Eq. (31)], then Eq. (39) should result in a self-consistent formulation for \( L(K_0+q) \). Kawasaki then showed that the conventional theory assumption that \( L(K_0) \) is slowly varying in the critical region is inconsistent with this equation, and therefore concluded that critical fluctuations in spin density drastically affect the Onsager kinetic coefficient and result in its divergence at the Curie point. In particular, he found for a ferromagnet \( (K_0 = 0) \) that a self-consistent solution of Eq. (28) requires that \( L(0) \) diverge as \( \chi^{3/4} \) at the Curie point. Therefore the diffusion constant again vanishes at the Curie point, but the rate is now \( \propto \chi^{-1/4} \), which is much slower than the \( \chi^{-1} \) dependence predicted by conventional theory, and is more in line with the critical behavior of \( \Lambda \) deduced from neutron experiments and the resonance data on nickel. By using the same formalism, this author obtained the seemingly consistent result that \( \Lambda(K_0) \propto \chi(K_0)^{-1/4} \) in an antiferromagnet, and consequently it might seem reasonable to make the general statement \( \Lambda(K_0+q) \propto \chi(K_0+q)^{-1/4} \) for small \( q \) in the critical region. However, Kawasaki points out that the new theory also predicts a strong dependence of the diffusion constant on wave vector and frequency of an applied disturbance,
so that generalizations must be made with caution. Also, the exponent of $X$ describing the divergence should not be taken too seriously in view of several simplifying approximations that were necessary in solving the self-consistent equation for $L(K_0+q)$. Therefore, the major contribution of this theory is just the qualitative result that the "staggered" diffusion constant goes to zero much more slowly than anticipated by conventional theory.

It is interesting to note the intrinsic difference between spin diffusion and the closely related problem of molecular diffusion in critical mixtures, where the conventional theory has proved adequate. The preceding theory was based on the expansion of the torque in terms of the macroscopic variables exhibiting critical fluctuations. In the case of molecular diffusion, however, Kawasaki shows that all the expansion coefficients vanish identically because of the time reversal transformation properties of the molecular diffusion current operator, and therefore $L$ remains finite at the critical point. Hence, Kawasaki has attributed the anomalous behavior of the diffusion constant in magnetic systems to the fundamental difference in the time reversal properties of the spin diffusion current operator.

At present there is no experimental data on magnetic crystals that either proves or disproves the above theory. Preliminary neutron investigations on RbMnF$_3$ indicate $\Lambda(K_0)$ goes to zero as $X^{-1/2}$, which is slower than that predicted by conventional theory but still faster than the Kawasaki prediction. Furthermore, even if the Kawasaki result were true it would still predict an observable, although smaller, anomaly in the antiferromagnetic resonance line width near $T_N$. Therefore, although this result
is helpful in understanding line widths, it is by no means the entire
answer and we must look further for a satisfactory explanation.

**Marshall Proposal**

Inelastic critical scattering of thermal neutrons close to elastic
peaks is the most direct way of studying the behavior of the spin-pair
correlation function. Measurement of scattering rates as a function of
momentum transfer \( q \) in the critical region provides direct information on
spatial spin correlation, while measurement of the energy distribution of
scattered neutrons for fixed \( q \) provides direct information on the decay
rate \( \Gamma_{K_0+q} \) of the \( q \)-th spontaneous fluctuation. The first type of experiment has well verified the Ornstein-Zernike description of spatial correlation as given by Eqs. (23) and (27). It was therefore surprising when measurements by Jacrot et al.\(^1\) of the energy spectrum of scattered neutrons from iron in the critical region indicated the decay rates \( \Gamma_{K_0+q} = \Delta q^2 \) were roughly independent of temperature, since conventional thermodynamics predicts correlation in time and space should increase together.

In considering this apparent contradiction, Marshall noticed that
little or no neutron data existed in the range \( q < \kappa \), where \( \kappa \) is the
inverse correlation distance. Since the minimum requirement for spin-wave-like propagation above the Curie temperature is \( q > \kappa \) (i.e., the wavelength of the excitation must be less than the extension of the local order), he suggested that neutron data in this range might well be more descriptive of magnetic excitations within correlated regions than of the non-propagating critical fluctuations assumed by conventional theory.

To illustrate how this effect might appear to lead to temperature independent decay rates in a ferromagnet we first consider the form of
the energy spectrum of scattered neutrons to be expected at various temperatures. In the low temperature limit it is well known that the spectrum consists of two sharp peaks at \( hq = \pm Aq^2 \), corresponding to the emission and absorption of spin waves, where \( A \) is the spin wave dispersion constant at \( T = 0 \). As the temperature is raised the spin waves get damped and the peaks become broadened into cutoff Lorentzians. There is also an energy renormalization due to spin wave interactions so that \( A \) is a function of temperature and gets smaller as the Curie point is approached. Then as we proceed through the transition temperature the spin wave peaks gradually diminish in intensity and spacing, and eventually merge into the single diffuse peak characteristic of high temperatures. Marshall has made a crude estimate of the separation between the spin wave peaks in iron at \( 0.8T_N \) and found it to be roughly the same as the width of the single scattering curve at infinite temperature. Therefore, if the intensity of scattering from propagating fluctuations (or "para-magnons") just above \( T_N \) is comparable to the diffuse scattering, then the width of the energy spectrum, which determines the decay rate, will remain roughly independent of temperature in the critical region. Furthermore, since both the high temperature width and the separation between spin wave peaks have a quadratic dependence on \( q \), the effective diffusion constant in the critical region will appear to remain constant for different values of \( q \), as deduced by Jacrot.

Recent high resolution scattering experiments\(^7\) on \( \text{RbMnF}_3 \) illustrate the merit of this suggestion. Figure 11 shows the energy spectrum in the critical region for \( q = 0.2\AA^{-1} \), where it is clearly evident the effects of propagating fluctuations are present well above \( T_N = 82.65^\circ\text{K} \). (As high as \( 94^\circ\text{K} \) there was still a suggestion of a triple peak for \( q = 0.2\AA^{-1} \).)
The results also indicate the existence of a quasi-elastic diffusive mode below $T_N$. The effective decay rates for various values of $q$ are shown in Fig. 12. Only for $q \approx 0$ is there evidence of critical slowing down, which was also the only case considered with $q < K$. For higher $q$ the decay rates are slowly varying with temperature and the $q$-dependence bears some resemblance to the dispersion relation for antiferromagnets $\omega_q = Aq$.

The effect of propagating fluctuations on linewidths in the critical region should also be dramatic. Collective excitations produce additional motion of the electronic spins that was not considered in our previous calculation of the effective modulation frequency of the dipolar interaction due to exchange. The neutron experiments indicate the mean modulation frequency associated with a given fluctuation is now approximately independent of temperature for finite $q$, rather than decreasing as $\chi(K_0 + q)^{-1}$. As we have already indicated, in a ferromagnet this implies the effective diffusion constant is independent of both temperature and wave vector (except $q = 0$), so that this theory provides a satisfactory explanation for the linewidth behavior observed in nickel. The seemingly inconsistent behavior of the diffusion constant in producing the strong $\chi_0/\chi$ dependence of the linewidth can now be understood as the special $q = 0$ case where the critical slowing down is not masked by collective excitations.

In antiferromagnets the agreement of theory with experiment is less satisfactory. The observed linewidths can be explained only if the decay rates $\Gamma_{K_0+q}$ are independent of both temperature and wave vector in the critical region, so that the effective modulation frequency $\tau_0^{-1}$ remains constant. Although independent of temperature, the decay rates have approximately a linear $q$ dependence, which can be attributed to the spin
wave dispersion relation in antiferromagnets. Since the probability of small q fluctuations increases rapidly in the critical region, this predicts a corresponding increase in $\tau_c$. However, now the dependence of $\Gamma_{K_0+q}$ on q is so weak that the integral of Eq. (38) does not converge, so that it is very difficult to accurately estimate this increase. By making the crude approximation that the Ornstein-Zernike form for $\chi(K_0+q)$ is valid over the first Brillouin zone and limiting the integral to this region we find $\tau_c \propto \log(q_{\text{MAX}}/k)$, which, in the range $1.002 < T/T_N < 1.02$ in K$_2$MnF$_3$, predicts a 40% increase in linewidth. This is considerably less than the factor of 5 increase predicted by conventional theory in the same range, but is still not consistent with the negligible variation in linewidth found experimentally. This lack of even a small variation of the linewidth with temperature cannot be understood within the limits of this theory.

Another apparent contradiction between this theory and experiment occurs in the interpretation of Heller and Benédek's nuclear resonance linewidth data on MnF$_2$ in the critical region. The linewidth can be attributed to fluctuations in the local hyperfine fields seen by the nuclei, and therefore can be directly related to the electron spin auto-correlation function, i.e., the linewidth in frequency units can be written

$$\Delta \omega \approx (\frac{A}{d^2}) \left[ \tau_z \langle S_z^2 \rangle + \frac{1}{2} \tau_x \langle S_x^2 \rangle + \frac{1}{2} \tau_y \langle S_y^2 \rangle \right]$$

where $A$ is the hyperfine coupling constant and $z$ defines the direction of the applied magnetic field. Therefore, as in the case of electron resonance, the linewidth is directly proportional to the mean lifetime $\tau$ of an electronic spin, which has been broken into components in this equation to consider the effect of crystal anisotropy. (However, now this result is
exact, while in the case of electronic resonance it was necessary to use a rather weak intuitive argument to relate $\tau_c$ to $\tau$. Furthermore, the nuclei cannot see the electronic spatial correlation, except indirectly through the time correlation.) In view of the previous discussion of the importance of propagating fluctuations on this lifetime, it was therefore surprising that the qualitative nature of the linewidth anomaly in MnF$_2$ in the critical region could be correctly described by the conventional theory of critical fluctuations.$^3$ Indeed, as predicted, the linewidth increased by a factor of 10 in the temperature interval $T-T_N \leq 1^0K$.

An obvious possible explanation for the success of conventional theory in this case would be a very low intensity of spin wave side bands in MnF$_2$ for all $q$ in the critical region, so that, as in the $q=0$ case, critical slowing-down would be the dominant effect. Pursuing this possibility we notice that the anisotropic behavior of the linewidth in MnF$_2$ can be attributed to the anisotropic behavior of the auto-correlation time. (MnF$_2$ is an easy axis antiferromagnet, and at $T_N$ the linewidth with the magnetic field parallel to this axis is nearly twice the linewidth with the field perpendicular to the axis.) In particular, it can be shown that in the broadening region ($T-T_N \leq 1^0K$) the easy axis correlation time is much longer than the transverse correlation time because of magnetic anisotropy, and therefore, from Eq. (42), a 2:1 linewidth ratio is predicted. (The importance of anisotropy on relaxation is discussed in more detail in Sec. VI.) Consequently, in determining the effective auto-correlation time in this region we are concerned only with the width of the energy spectrum of scattered neutrons due to fluctuations along the easy axis. But we know we cannot possibly associate spin wave processes with longitudinal fluctuations$^6$ and
therefore the width of this energy spectrum should behave according to the dictates of conventional theory, as predicted by the linewidth data.

Existing neutron scattering data on MnF$_2$ is too crude to check this hypothesis. However, high resolution experiments are anticipated in the near future$^{40}$ that will use the anisotropic properties of this crystal to separately observe the energy spectrum of the longitudinal and transverse fluctuations in the critical region. To further clarify this problem, it would be of interest to do nuclear resonance linewidth studies of RbMnF$_3$ in the critical region, since the importance of propagating fluctuations is well established in this crystal.

Conclusions

Existing experimental data on electron relaxation in cubic ferro- and antiferromagnets is inconsistent with the predictions of conventional theory. However, by introducing recently proposed modifications to this theory, reasonable agreement with experiment can be obtained in certain cases. Of the two possible modifications, the Marshall suggestion is the most important for understanding linewidths in cubic crystals. In the first place, it provides the best explanation for the observed linewidths. Secondly, its basic contention that propagating fluctuations can exist above $T_N$ has been experimentally verified, while at present there is no such evidence in support of the Kawasaki proposal. Finally, even if both modifications were simultaneously present, the Kawasaki effect would be completely dominated by the presence of collective excitations, as indicated by the neutron data on RbMnF$_3$. 
Unfortunately, even with these modifications, our relaxation theory still predicts at least a slowly varying temperature dependence of the line-width in cubic antiferromagnets, which is not observed in either RbMnF$_3$ or KMnF$_3$. The $\chi_0/\chi$ dependence alone roughly predicts a 25% increase as the critical point is approached, and it is difficult to believe the cumulative effect of all such slowly varying terms in our relaxation expression would exactly cancel in both crystals. This is the major failure of our theory, and suggests that perhaps the whole problem of spin relaxation in antiferromagnets should be considered from a different point of view.

VI. RELAXATION IN ANISOTROPIC ANTIFERROMAGNETS; $T \geq T_N$

A. Theory

The existence of anisotropy in an antiferromagnet considerably complicates the theory of spin relaxation presented in the preceding section. That the presence of anisotropy can drastically affect magnetic relaxation in the critical region is dramatically illustrated by comparing the sharp linewidth singularity observed in hexagonal CsMnF$_3$ with the corresponding negligible linewidth variation observed in both cubic RbMnF$_3$ and KMnF$_3$. Indeed, a broadening of the resonance line with a corresponding reduction in absorption as the transition temperature is approached from above seems to be a characteristic of all noncubic antiferromagnets. At first sight it might seem surprising that a relatively small amount of anisotropy could produce such large effects. However, because of the special nature of the coupling between exchange and anisotropy in antiferromagnets the "effective" magnetic field due to the anisotropy is often considerably magnified. For example, as we saw in Sec. III, the high frequency resonance mode sees an
additional resonance field due to anisotropy of order \( (2H_e H_a)^{1/2} \). Another example of this is the magnitude of an external field required to rotate the sublattice magnetizations away from the preferred direction in an antiferromagnet, as opposed to a ferromagnet. Again, this so-called "flop-field" is of order \( (2H_e H_a)^{1/2} \), while in a ferromagnet the applied field need only be of order \( H_a \). For this reason, both the size and lifetime of critical fluctuations are considerably modified by the presence of anisotropy, although the anisotropy field is usually two orders of magnitude smaller than the exchange field.

The best way of characterizing anisotropy in critical fluctuations is with the wave number-dependent tensor susceptibility \( x^{AB}(k) \) introduced in Sec. V. We now define \( x_{||}(k) \) and \( x_{\perp}(k) \) respectively as the susceptibilities parallel and perpendicular to the crystal direction defined by the anisotropy field. Then from Eq. (28), we can define \( (K_{||})^{-1} \) and \( (K_{\perp})^{-1} \) as the corresponding correlation lengths. Therefore, as before, the probability and lifetime of a fluctuation in a given direction are determined by the corresponding behavior of the susceptibility in that direction through Eqs. (26) and (31).

To illustrate the effect of anisotropy on fluctuations we consider the case of MnF\(_2\). This crystal is an easy axis antiferromagnet with \( T_N = 67^\circ K \), \( H_a \approx 9 \times 10^3 \) Oe, and \( H_e \approx 5.5 \times 10^5 \) Oe. Then both theory\(^2\) and experiment\(^3\) predict \( x_{||}(K_o) \) diverges at \( T_N \), but \( x_{\perp}(K_o) \) behaves as if it were diverging at a lower temperature \( T_{\perp} \) where \( T_N - T_{\perp} = 1.4^\circ K \). Therefore, the probability, correlation length, and lifetime of transverse fluctuations in the critical region are negligible when compared to the corresponding probabilities of longitudinal fluctuations. This result can be understood qualitatively through
the following argument. As was mentioned above, an effective field of order \((2H_e H_a)^{1/2}\) is necessary to rotate the sublattice magnetizations away from the easy direction. Therefore, we can picture transverse fluctuations as being inhibited by this field. Now it is well known that the effect of an applied field \(H\) on an antiferromagnet in the temperature region about \(T_N\) is to reduce \(T_N\) by an amount proportional to \(H^2\). In the molecular field approximation the fractional change can be written as \([\frac{T_N - T_H}{T_N}] \approx \frac{(H/H_e)^2}{2}\). Consequently, since \((2H_e H_a)^{1/2}\) acts like an externally applied field with respect to transverse fluctuations, we have \([\frac{T_N - T_I}{T_N}] \approx \frac{(2H_e H_a)^{1/2}/H_e}{2}\) \(\approx 0.03\), which implies \(T_N - T_I \approx 2^\circ K\).

With these modifications to our previous theory of critical fluctuations we are now in a position to construct a theory of linewidths in anisotropic crystals. Mori and Kawasaki have considered this problem in detail, and the following discussion will essentially trace their analysis. Their first step was to simplify the problem by assuming the total anisotropy, both crystalline and dipolar, could be expressed in the form of a single ion anisotropy energy \(H_A = D S_i^2\), where \(D\) is the anisotropy constant. (We have assumed the applied field is parallel to the anisotropy axis so that our system has axial symmetry and therefore the general damping expression, Eq. (12), applies.) Since the dominant anisotropy mechanism is dipolar for the crystals considered in this paper, we expect \(D\) to be highly temperature dependent. Actually, as was discussed in Sec. IV, when the effect of the external field is considered, the effective anisotropy constant in \(CsMnF_3\) changes sign in the critical region. We therefore assume for this analysis that we are close enough to the transition temperature that the mean correlation length is large compared with the radius of convergence of the dipole-dipole sum,
so that $D$ is approximately temperature independent. Since the experimentally
determined rate of convergence is rapid in $CsMnF_3$ this is not a serious
restriction. For further simplicity, we assume anisotropy is the only line
broadening mechanism, since the contribution of isotropic dipolar inter-
actions has already been considered in the preceding section. Then the system
Hamiltonian is written

$$
\mathcal{H} = \gamma \hbar \Sigma_{i} S_{i}^{z} - \Sigma_{i,j} J_{ij} S_{i} \cdot S_{j} + D \Sigma S_{i}^{z}^{2}
$$

(43)

Then, as before, the damping can be written

$$
\Gamma_{o}^{\pm} = \frac{1}{N} \frac{3}{S(S+1) \gamma^{2} \hbar^{2}} \left( \frac{\chi}{\chi_{c}} \right) \tau_{c} \langle [f_{+}^{\pm}, f_{-}^{\pm}] \rangle
$$

(44)

where

$$
f_{+}^{\pm} = \mp 2i \gamma D \sum_{i} (s_{i}^{z}, s_{i}^{\pm})
$$

(45)

and $\tau_{c}$ is defined by Eq. (18). This expression can be simplified with the
aid of the pair approximation, i.e.,

$$
\langle [f_{+}^{\pm}, f_{-}^{\pm}] \rangle \approx N(2\gamma D)^{2} \left[ \langle s_{1}^{z} \rangle^{2} \langle s_{1}^{+}, s_{1}^{-} \rangle + \sum_{j \neq 1} \langle s_{j}^{z} s_{j}^{\pm} \rangle \langle s_{j}^{+}, s_{j}^{-} \rangle \right]
$$

(46)

Since only the second term in the brackets describes correlation between
different spins, it is the only one with a strong temperature dependence
in the critical region. Using the Ornstein-Zernike expression for pair
correlation, Eq. (27), and converting the summation to an integral we have

$$
\langle [f_{+}^{\pm}, f_{-}^{\pm}] \rangle \propto \left[ 1 + \frac{A \exp[-\lambda(K_{\parallel}+K_{\perp})r_{\perp}]}{(K_{\parallel}+K_{\perp})r_{\perp}} \right] (T \rightarrow T_{N})
$$

(47)

where $A$ and $\lambda$ are numerical constants $= 1$. We therefore have the inter-
esting result that linewidths are quite sensitive to spatial correlation
in anisotropic crystals. Such an effect is intuitively reasonable if we picture \(-\mathbf{D}_1^z\) as the local field seen by the spin \(S_1\). Then one effect of anisotropy is to increase the probability of fluctuations in the \(z\)-direction, thereby increasing the root-mean-square value of this local field, and hence, broadening the line. It is also of interest to note that this result predicts the line width does not diverge at \(T_N\), since \(K_1\) remains finite at the critical point. However, this result is questionable since in the immediate vicinity of \(T_N\) the Ornstein-Zernike form, pair-approximation, etc. are no longer good approximations.

It is tempting to again assume \(\tau_C\) is effectively the mean lifetime of a single spin as determined by exchange, using the simple intuitive argument of Sec. V. However, the situation is now more complicated for rather obscure reasons. For instance, the Mori continued-fraction representation given by Eq. (37) now predicts a strong temperature dependence for \(\tau_C\) due to its direct dependence on \(\langle f^+ f^- \rangle\). (In the isotropic case \(\langle f^+ f^- \rangle\) was slowly varying and therefore no temperature dependence was predicted for \(\tau_C\).) This result suggests the singularity in \(\tau_C\) is enhanced by the presence of anisotropy, and emphasizes the danger of relying heavily on intuitive arguments. Therefore, in view of our inability to understand the behavior of \(\tau_C\) in even the simple isotropic case, a theoretical prediction for its actual temperature dependence is considered beyond the scope of this paper. However, we do have the consistent qualitative prediction of all theories that \(\tau_C\) increases rapidly near \(T_N\) in anisotropic crystals, and therefore we expect the linewidth singularity to reflect increases in both time and spatial correlation.
B. Comparison with Experiment

Mori and Kawasaki developed the above theory for the express purpose of explaining the linewidth singularity in MnF$_2$. Using the continued-fraction representation for $\tau_c$ they obtained reasonable quantitative agreement with experiment in the temperature region $T/T_N > 1.02$. The importance of spatial correlation on the linewidths was very evident since the broadening region was $T - T_N \leq 10^6K$, as opposed to $T - T_N \leq 1^6K$ for the corresponding NMR linewidths, which are insensitive to spatial correlation. Unfortunately, no careful experimental work has been done in the interesting temperature region closer to $T_N$. Strandberg and Burgiel have studied the the EPR linewidth of MnF$_2$ in the critical region with the field parallel and perpendicular to the anisotropy axis, and observed approximately a 3:1 linewidth ratio. However, as is discussed in Appendix I, the simple scalar expression for damping, Eq. (12), is valid only for spin systems with uniaxial symmetry about the direction of the applied field. For this reason damping with the field perpendicular to the anisotropy axis has not yet been considered theoretically, and we are again forced to use intuitive arguments. Strandberg and Burgiel suggested that the principle mechanisms producing anisotropy in the linewidth were similar in both the NMR and EPR cases, so that the electron linewidth should reflect the NMR behavior, where a 2:1 ratio of the parallel to perpendicular linewidths has been verified both theoretically and experimentally. The theoretical prediction of this ratio is based on the argument that fluctuations in magnetization in a direction perpendicular to the applied field are only half as effective in broadening the line as fluctuations in magnetization parallel to the applied field. (This is a general property of spin-spin interactions,
and is related to the two roughly equal, but distinct, line broadening mechanisms of like spins, often described as the secular and non-secular contributions. This result is described mathematically by Eq. (42) of Sec. V, from which it is obvious that if fluctuations predominate in one direction then a 2:1 ratio is predicted. That the situation should be similar in the EPR case is not obvious, especially in view of the importance of spatial correlation, although the experimental results are not inconsistent with such a hypothesis.

Since CsMnF$_3$ is a hard-axis antiferromagnet, it would seem to be a good crystal on which to check this hypothesis. In particular, since the predominant fluctuations are now transverse to the anisotropy axis, the same arguments predict a 2:3 ratio for the parallel to perpendicular linewidth in the critical region. Unfortunately, as we saw in Sec. IV, there are apparently inhomogeneous broadening mechanisms in CsMnF$_3$ that completely mask the intrinsic behavior of the linewidths in the critical region, so that this ratio cannot be checked.

In making further comparisons of the linewidth singularity of CsMnF$_3$ with theory, we see from Fig. 4 that there is no $\chi'_0/\chi$ slowly varying broadening of the perpendicular linewidth, as predicted by Eq. (33). This absence of a $\chi'_0/\chi$ dependence is consistent with the experimental results on cubic antiferromagnets, although there seems to be such a dependence in MnF$_2$. However, the general linewidth behavior of CsMnF$_3$, as well as qualitatively similar results on the hard axis antiferromagnets CsMnCl$_3$ and RbMnCl$_3$, bear out this section's major prediction of the importance of spatial correlation on linewidths in anisotropic crystals.
VII. ACKNOWLEDGMENTS

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Fig. 1: Microwave cavity and temperature control unit.
Space group: $P6_3/mmc$

$\begin{align*}
\frac{1}{2}c \\
a &= 6.213 \text{ Å} \\
c &= 15.074 \text{ Å}
\end{align*}$

Fig. 2: Half of the chemical cell of CsMnF$_3$. 
Fig. 3: Field dependent resonance modes in CsMnF$_3$. 

**Low-frequency mode**

**High-frequency mode**
Fig. 4: Temperature dependence of the electron resonance line width in CsMnF$_3$ from 40 K to 300 K with the applied field perpendicular to the c axis.
Fig. 5: Line widths and resonance fields in CsMnF$_3$ in the critical region for two crystal orientations. The numbers in parentheses are the resonance fields of the high frequency mode.
Fig. 6: Asymmetric behavior of the derivative resonance curves of CsMnF$_3$ in the critical region.
Fig. 7: Doubly logarithmic plot of the line widths in CsMnF$_3$ vs.
$T - T_N$, where we have arbitrarily chosen $T_N = 51.85^\circ\text{K}$. 

$H_0 \parallel c$ axis

$H_0 \perp c$ axis

$T_N = 51.85^\circ\text{K}$
Fig. 8: Temperature dependence of the resonance fields in CsMnF$_3$ between 75°K and 150°K. Fig. 8b compares the experimental and theoretical predictions for the temperature dependence of the anisotropy field $H_a(T)$. 

\[ H_a(T) = \left( H_a(0) / M(0) \right) \chi(T) H_0 \]
Fig. 9: Electron resonance line widths in RbMnF₃ and KMnF₃ in the critical region.
Fig. 10: The relaxation frequency $\tau^{-1}$ vs. temperature of nickel in the paramagnetic region (from Salamon).
Fig. 11: Inelastic scattering at $q = 0.2 \text{ Å}$ in RbMnF$_3$ at various temperatures near the Neél point (from Nathans, Menzinger, and Pickart).
Fig. 12: Widths of the inelastic scattering in RbMnF₃ at various q values as a function of temperature (from Nathans, Menzinger, and Pickart).
In this appendix we will discuss in more detail than in the text the Mori and Kawasaki\textsuperscript{27} formalism for the spin damping in ferro- and antiferromagnets. In considering damping phenomena we are usually interested in the long time behavior of the relaxation function

\[ \Phi(t) = [A(t), A^*]/(A,A^*) \]  \hspace{1cm} (A.1)

where \( A(t) \) denotes the deviation of the macroscopic dynamic variable of interest from its mean value (so that \( \langle A \rangle = 0 \)), and

\[ (A,B) = \int_0^\beta d\lambda \langle Ae^{-\lambda H} Be^{\lambda H} \rangle \]  \hspace{1cm} (A.2)

for arbitrary \( A \) and \( B \), where \( \beta = 1/k_B T \) and \( H \) is the system Hamiltonian. To study \( \Phi(t) \) we first look at the equation of motion of \( A(t) \), which can be written

\[ \frac{d}{dt} A(t) = F_e(t) + F(t) \]  \hspace{1cm} (A.3)

where \( F_e(t) \) represents externally applied forces and \( F(t) \) describes the internal system forces responsible for any intrinsic collective motion and the damping (e.g., in the case of a particle experiencing Brownian motion, \( A(t) \) is the particle momentum, \( F_e(t) \) is a force like gravity, and \( F(t) \) represents molecular collisions). It is well known\textsuperscript{44} \( F(t) \) can be split into the sum of a slowly varying force and a randomly fluctuating force. Mori\textsuperscript{28} has considered this problem in detail and was able to derive the following exact equation of motion for \( A(t) \):

\[ \frac{d}{dt} A(t) - i \Omega A(t) + \int_0^t \rho(t-s) A(s) ds = f(t) \]  \hspace{1cm} (A.4)
where $\Omega$ is a frequency describing the collective oscillation of $A(t)$ and is defined by

$$i\Omega = \left[ \frac{d}{dt} \Phi(t) \right]_{t=0} = \frac{\langle \dot{A}^*, A^* \rangle}{\langle A, A^* \rangle}$$  \tag{A.5}

and $f(t)$ is a purely random force whose time correlation function is connected with the damping function $\rho(t)$ by

$$\rho(t) = \langle f(t), f^*(t) \rangle / \langle A, A^* \rangle.$$  \tag{A.6}

$f(t)$ differs from the total internal system force $F(t)$ in two respects. First, $f(0)$ does not contain that part of $F(0)$ that produces a collective oscillation, which is seen by comparing (A.3) and (A.4) at $t = 0$. Therefore, $\langle f, A^* \rangle = 0$, and $f(0)$ describes fluctuations about the collective oscillation. Secondly, the time evolution of $f(t)$ is governed by a special propagator that differs from the usual Heisenberg operator describing the time evolution of mechanical quantities. It is this difference that insures $f(t)$ does not contain a slowly varying part, and is truly a randomly fluctuating force completely uncorrelated with $A(t)$, i.e., $\langle f(t), A^* \rangle = 0$.

The third term on the left of (A.4) is, therefore, the slowly varying force (i.e., the friction force with "memory") which is written as a functional of $A(s)$, $t \geq s \geq 0$, since in general we would expect its value to depend on the past history of $A(t)$.

Equation (A.4) is identical with the Langevin equation of motion is the slowly varying term is replaced by $\Gamma A(t)$, where $\Gamma$ is the damping constant of $A(t)$. This is equivalent to requiring the damping function to take the form $\rho(t) = 2 \Gamma \delta(t)$, which Mori shows is a good approximation if and only if the correlation time $\tau_c$ of $\rho(t)$ is much shorter than $\Gamma^{-1}$.
Within this approximation, (A.4) and (A.6) can be integrated to yield

\[ \phi(t) = e^{(\text{i}\Omega - \Gamma)t} \quad (t >> \tau_c) \]  \hspace{1cm} (A.7a)

\[ \Gamma = \text{Re}(\Gamma') = \text{Re} \int_0^\infty \text{dt} \quad e^{-\text{i}\Omega t} \frac{\phi(t)^*}{(A_1 A_2^*)} \quad (\Gamma_c << 1) \]  \hspace{1cm} (A.7b)

So far we have considered the case of only one variable, \( A(t) \). In magnetic systems, however, it is necessary to deal with the relaxation of all three components of magnetization simultaneously, since they are often strongly coupled. The extension of Eq. (A.7) to this many variable cases is straightforward if we redefine \( A(t) \) as a three-dimensional column matrix composed of the three components of magnetization \( M_x, M_y, \) and \( M_z \). Then \( \phi(t), \Omega, \Gamma, \) etc. are \( 3 \times 3 \) matrices and Eqs. (A.1) to (A.7) are assumed to obey the ordinary rules of matrix multiplication. However, now the expression for the damping of a component of magnetization is considerably more complicated because of the matrix relationship coupling the variables. Mori has shown that in the special case of a spin system with axial symmetry about the \( z \)-axis (we assume the \( z \)-direction is defined by a weak external magnetic field) we can, to a good approximation, assume \( \Gamma \) is a diagonal matrix when referred to the normal modes of the system. Then the damping constant of one of the normal modes is just the corresponding diagonal element of the damping matrix, and is given by the scalar relationship of Eq. (A.7). The expression for the damping of the transverse component of total magnetization in an axially symmetric system (normal modes are \( M^\pm = M_x \pm \text{i}M_y \)) is therefore given by
\[ \Gamma^\pm = \text{Re} \int_0^\infty dt \, e^{-i\Omega t} (f^+(t), f^-)/(M^+, M^-) \quad (\Gamma \tau_c \ll 1) \quad (A.8) \]

where, from Eq. (A.4), we see \( f^\pm = M^\pm \mp i \Omega M^\mp \). When the temperature region of interest is not too low (i.e., \( \hbar \Omega \ll k_B T \)), it is a good approximation to replace the relaxation functions with \((k_B T)^{-1}\) times the corresponding correlation functions, i.e.,

\[ \Gamma^\pm = \text{Re} \int_0^\infty dt \, e^{-i\Omega t} \langle [f^+(t), f^-]/(M^+, M^-) \rangle; \quad (\hbar \Omega \ll k_B T) \quad (A.9) \]

which is Eq. (12) of the text.

The above results can be further generalized to describe relaxation of those Fourier components of the magnetization that are approximate constants of the motion (in the sense \( \Gamma \tau_k \ll 1 \), where \( k \) is the wave vector). For \( k \) close to a magnetic reciprocal lattice vector \( K \), this is a good approximation in both ferro- and antiferro-magnets, and we have

\[ \langle [s^{\alpha}(t), s^{\beta*}(t)] \rangle = \langle [s^{\alpha}, s^{\beta*}] \rangle \, e \left( i \Omega - i \kappa \right) t \quad (t >> \tau_k) \quad (A.10a) \]

where

\[ \Gamma^{\alpha \beta}_k = \text{Re}(\Gamma^{\alpha \beta}_k) = \text{Re} \int_0^\infty dt \, e^{-i\Omega t} \langle [f^{\alpha}(t), f^{\beta*}(t)]/\langle [s^{\alpha}, s^{\beta*}] \rangle \rangle \quad (\Gamma \tau_k \ll 1) \quad (A.10b) \]

where we have used the relation \( s^{\alpha}_k = (\gamma^\alpha \hbar^2)^{-1/2} M^{\alpha}_k \), and redefined the torque as \( f^\pm_k = s^{\pm}_k \mp i \Omega \kappa s^{\pm}_k \) to obtain this form.
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