Critical Electron-Paramagnetic-Resonance Spin Dynamics in $NiCl_2$

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We have studied the critical behavior of the electron-paramagnetic-resonance linewidth in the planar XY antiferromagnet $NiCl_2$; it is found that the linewidth diverges like $\xi \sim (T - T_N)^{-0.7}$ rather than $\xi^{5/2}$ predicted by the current random-phase-approximation theory.

In a near-Heisenberg antiferromagnet the long-wavelength spin-fluctuation decay rate contains contributions both from exchange-induced spin diffusion and from anisotropy-induced spin-spin relaxation.[1,2] The spin-diffusion term has the familiar form DQ^2 with $D \propto \xi^{-1/2}$, where ξ is the correlation length, while current theory[1,2] predicts that the spin-spin relaxation rate $1/T_2$ should diverge like $\xi^{5/2} \sim (T - T_N)^{-5/3}$. This $\xi^{5/2}$ behavior for $1/T_2$ is expected to hold only for $\tau = T/T_N - 1 > H_A/H_E$, where H_A, and H_E are the anisotropy and exchange fields, respectively. Ideally, therefore, H_A/H_E should be as small as possible in order to maximize the reduced temperature range over which the $1/T_2 \sim \xi^{5/2}$ critical behavior should hold. Recent neutron-scattering studies[3] on the planar antiferromagnet $NiCl_2$ have indicated that it is an ideal candidate for such studies. In addition, previous electron-paramagnetic-resonance (EPR) measurements[4] on $NiCl_2$ have indicated particularly interesting linewidth behavior. In this Letter we report a detailed EPR study of the $Q = 0$ spin-spin relaxation rate in $NiCl_2$ with special emphasis on the critical region. We find that the general aspects of the theory for EPR critical linewidths are confirmed, including the dependence of the EPR linewidth ΔH ($\propto 1/T_2$) on field angle, the ultimate finiteness of ΔH at T_N, and, less definitely, the crossover from the fast to slow fluctuation regimes. However, the actual divergence of ΔH is significantly weaker than that predicted by the random-phase-approximation (RPA) theory, thus indicating a fundamental failure in that theory. Outside of the critical region we observe a crossover from a narrowing to a diverging regime in ΔH as T_N is approached. This is interpreted as a changeover from predominantly two-dimensional ferromagnetic fluctuations to three-dimensional antiferromagnetic behavior.

$NiCl_2$ has the hexagonal $CdCl_2$ crystal structure, space group D_{3d}^5, which is composed of layers of Ni^{++} ions separated by two intervening Cl^- layers. Below $T_N = 49.5$ K, the Ni^{++} spins order ferromagnetically within the planes with the spins perpendicular to the hexagonal c axis and with successive planes oriented antiferromagnetically with respect to each other. The Ni^{++} ($S = 1$) spin Hamiltonian contains a Zeeman term with $g = 2.24$, an isotropic exchange term with in-plane exchange integrals[3] $J_{nn} = -43.8$ K, $J_{nnn} = 9.8$ K ($\mathcal{H}_{ij} = J\vec{S}_i \cdot \vec{S}_j$), a nearest-neighbor between-plane exchange $J_{nn}' = 1.6$ K, and an anisotropy term $\mathcal{H}_A$. The latter term contains contributions from single-ion anisotropy, anisotropic exchange, and magnetic-dipole interaction; in $NiCl_2$ all three contributions are expected to be comparable. Spin-wave measurements[5] give a net anisotropy field $g\mu_B H_A^z = 0.8$ K with the sign such that the spins lie in the plane. In mean-field theory this XY anisotropy corresponds to a shift in reduced ordering temperature $(T_N^{x,y} - T_N^z)/T_N^{x,y} = 0.004$. This is significantly smaller than in other antiferromagnets such as MnF_2 where, for example, from the work of Schulhof *et al.*[5] $(T_N^{\parallel} - T_N^{\perp})/T_N^{\parallel} = 0.04$. Thus, $NiCl_2$ should provide a more accurate test of the theory for ΔH in the critical region.[5]

We consider first the experimental technique and results. The samples were typically circular platelets 3 mm in diameter and ~0.1 mm thick with the hexagonal c axis perpendicular to the flat face. The measurements reported in this paper were carried out mainly at 17.59 GHz using a conventional homodyne spectrometer. At room temperature a symmetric isotropic Lorentzian resonance line with $g = 2.24$ and $\Delta H = 680$ G is observed. The linewidths as a function of temperature for $H \parallel c$ and $H \perp c$ are shown in Figs. 1 and 2. For $T > 49.5$ K the lines are all accurately

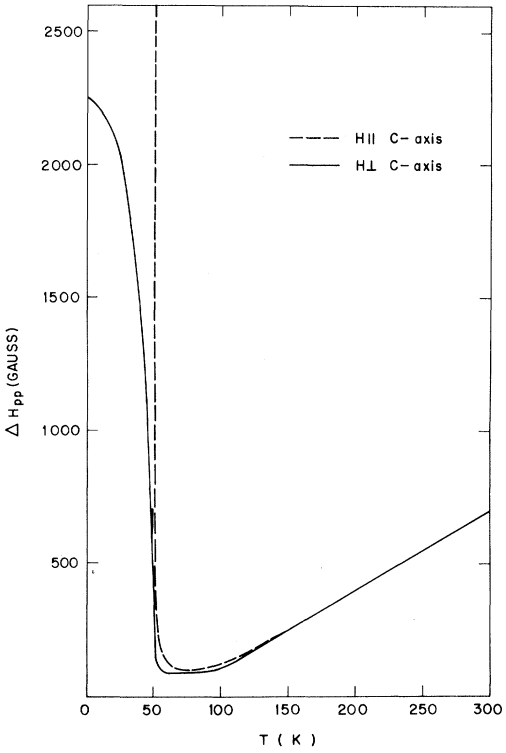

FIG. 1. Derivative peak-to-peak EPR linewidths ΔH_{pp} in $NiCl_2$ at 17.59 GHz as a function of temperature: 0–300 K.

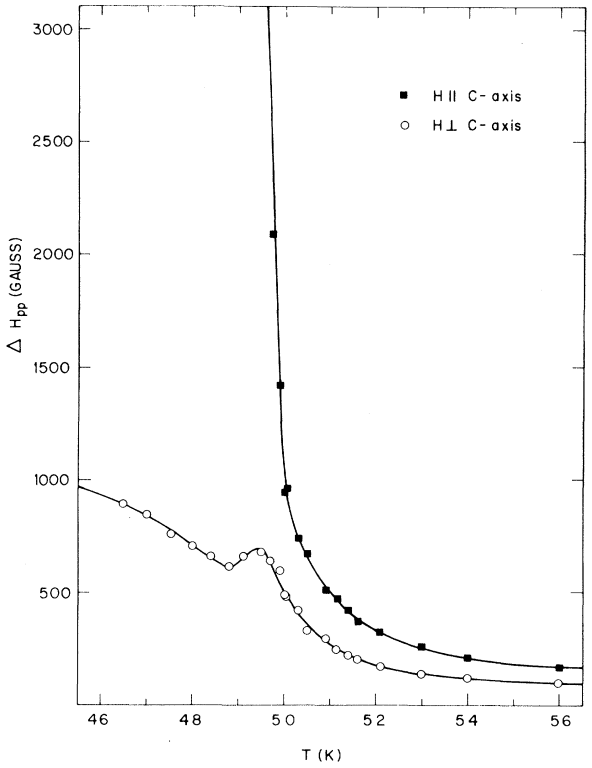

FIG. 2. Derivative peak-to-peak EPR linewidths ΔH_{pp} in $NiCl_2$ at 17.59 GHz: 46–56 K.

Lorentzian out to at least several half-widths. For $T < T_N$ no resonance is observed for $H \| c$, but for $H \perp c$ the XY antiferromagnetic resonance (AFMR) mode is readily observable down to 1.7 K.

As is evident in Figs. 1 and 2, the resonance line narrows continuously as the temperature is reduced below 295 K with ΔH becoming anisotropic below ~ 150 K. The linewidth reaches a minimum at 65–70 K, and then increases rapidly both for $H \| c$ and $H \perp c$. Between 60 and 50 K, $\Delta H_{\|}/\Delta H_{\perp} \sim 2$. $\Delta H_{\perp}$ reaches a maximum of 680 G at 49.5 K, while $\Delta H_{\|}$ increases to about 3000 G at 49.5 K beyond which no resonance signal can be seen. The results are presented in log-log form in Fig. 3. Here we take $T_N = 49.5$ K, the temperature at which $\Delta H_{\perp}$ reaches its local maximum value (see Fig. 2) and below which no resonance can be seen for $H \| c$. In the reduced temperature range $0.004 \leq \tau \leq 0.25$, $\Delta H_{\|}$ follows a simple power law with an exponent -0.7; $\Delta H_{\perp}$ follows this same power law down to $\tau = 0.01$, but deviates markedly from power-law behavior below $\tau = 0.01$.

Clearly, the EPR linewidths in $NiCl_2$ exhibit richly detailed behavior which should be explainable using current theory. As mentioned previously, the fundamental quantity involved is the *zero-field spin-spin relaxation time* which for Lorentzian lines can be written quite generally as[6]

$$1/T_2^{\alpha} = \chi_T^{\alpha-1} \int_0^{\infty} dt \, (\dot{M}^{\alpha}(t), \dot{M}^{\alpha}(0)), \qquad (1)$$

where $M^{\alpha} = g\mu_B \sum_i S_i^{\alpha}$, $\chi_T^{\alpha} = (M^{\alpha}, M^{\alpha})$, and $(,)$

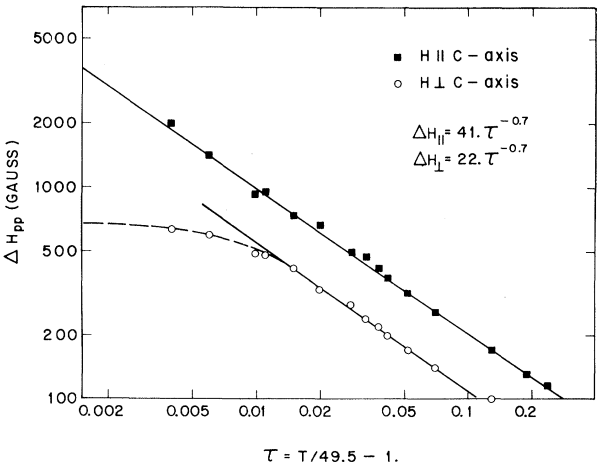

FIG. 3. Log-log plot of ΔH_{pp} versus reduced temperature in $NiCl_2$.

is the usual relaxation function. The relaxation function $(\dot{M}^{\alpha}(t), \dot{M}^{\alpha}(0))$ in Eq. (1) involves time-dependent four-spin correlation functions which for a system with weak XY anisotropy are typically of the form $(S_i^{\parallel}(t)S_j^{\perp}(t), S_k^{\parallel}(0)S_l^{\perp}(0))$, where $\parallel, \perp$ refer to the z axis (the hexagonal c axis in $NiCl_2$). Because of the difficulty of treating such four-spin relaxation functions, existing theories[1,2] factorize them into the product of two two-spin relaxation functions via the RPA. With the assumptions (a) the fluctuations being isotropic in spin space [in $NiCl_2$ this limits one to reduced temperatures much greater than $(T_N^{x,y} - T_N^{z})/T_N^{x,y} = 0.004$]; (b) the dominant contribution to $1/T_2$ in the critical region coming from the region in q space around the superlattice position $\vec{K}_0$; (c) a uniaxial anisotropy tensor with $u_{xx}(\vec{K}_0) = u_{yy}(\vec{K}_0) = u_{\perp}$, $u_{zz}(\vec{K}_0) = u_{\parallel}$; (d) the RPA factorization, one finds for the critical part of the zero-field spin-spin relaxation time.

$$(1/T_2)_{\text{crit}} = (C/\chi_T)(u_{\parallel} - u_{\perp})^2 \sin^2\theta \sum_{\vec{q}} \int_0^{\infty} dt\, (S(\vec{q}+\vec{K}_0, t), S(\vec{q}+\vec{K}_0, 0))^2 \qquad (2)$$

for spin fluctuations along a direction making an angle θ with respect to the z axis. Near the critical point

$$(S(\vec{q}+\vec{K}_0, t), S(\vec{q}+\vec{K}_0, 0)) \propto \exp[-\Gamma(q)t](1/\xi^2 + q^2)^{-1},$$

where according to dynamic scaling[7] $\Gamma(q) \propto \xi^{-3/2} \times f(q\xi)$. Substitution in Eq. (3) yields immediately $(1/T_2)_{\text{crit}} \propto \xi^{5/2}$.

In an EPR experiment in which the relaxation rate $\Gamma(0)$ is much greater than the microwave frequency, the linewidth is simply proportional to $1/T_2$ averaged over the plane perpendicular to $\vec{H}$. Here we neglect any intrinsic modification of the spin fluctuations by the field, an approximation which would appear to be valid in an antiferromagnet. Thus, for $h\nu/\Gamma(0) \ll 1$, one finds

$$\Delta H_{\parallel}(\text{crit}) = 2\,\Delta H_{\perp}(\text{crit}) = B(u_{\parallel} - u_{\perp})^2 \xi^{5/2}, \qquad (3)$$

where B is slowly varying near T_N. In the region $h\nu/\Gamma(0) \gg 1$, where only the secular terms in $\mathcal{H}_A$ contribute, $\Delta H_{\parallel}$ is unchanged from Eq. (3) while $\Delta H_{\perp}$ is simply reduced by a factor of 2. Finally, for $\tau \lesssim 0.004$ in $NiCl_2$ the isotropic approximation in Eq. (2) should fail so that the time dependence will be dominated by the noncritical component; $\Delta H_{\parallel,\perp}$ should then ultimately be finite at T_N.

We now compare this theory with our experimental results in $NiCl_2$. For $0.01 \lesssim \tau \lesssim 0.2$, $\Delta H_{\parallel}/\Delta H_{\perp} \simeq 2$ as expected from Eq. (4); this concomitantly implies that the noncritical contribution is small; for $\tau < 0.01$ the ratio increases. This may be readily interpreted to imply that at $\tau \sim 0.01$, $NiCl_2$ passes from the $h\nu/\Gamma(0) < 1$ to the $h\nu/\Gamma(0) > 1$ regime; this crossover should manifest itself only in $\Delta H_{\perp}$ as observed experimentally. Direct measurements of $\Gamma(0)$ do not exist in $NiCl_2$. However, in the Heisenberg antiferromagnet $RbMnF_3$,[8] $\Gamma(0) = 17.5$ GHz at $\tau \sim 0.015$ in good accord with our value of 0.01. Finally, we note that $\Delta H_{\perp}$ is finite at T_N as anticipated. It should be emphasized that all of the above results rest only on symmetry and general critical slowing down considerations, that is, assumptions (a)–(c), and are independent of the RPA factorization made in arriving at Eq. (3).

We now consider the observed exponent; for $0.004 \lesssim \tau \lesssim 0.25$, we have $\Delta H_{\parallel} \propto (T - T_N)^{-0.7}$. In systems with Heisenberg symmetry in three dimensions such as $RbMnF_3$,[8] one finds typically $\xi \propto (T - T_N)^{-0.70}$. Thus in $NiCl_2$ we have $\Delta H_{\parallel} \propto \xi$ rather than the $\xi^{5/2}$ behavior predicted by the RPA theory. Least-squares fits to the data using varying ranges of reduced temperature and varying weighting factors indicate that the exponent -0.7 is inviolate. We must conclude that our results in $NiCl_2$ indicate a fundamental failure of the RPA theory. It is difficult to ascertain unambiguously the explicit reason for the breakdown of the theory although the good agreement obtained otherwise suggests that the difficulty rests in the RPA factorization of the four-spin correlation function. We should note also that in a less-detailed study at 9 GHz, Lozenko and Ryabchenko[4] find exponents of -0.5 to -0.6, which illustrates at the minimum that the magnitude of the exponent does not increase with decreasing microwave frequency.

To conclude we consider the precritical region $\tau > 0.25$ in $NiCl_2$. In ferromagnets and ferrimagnets for $\tau > 0.25$ the linewidth is dominated by the strongly divergent factor χ_T in Eq. (2) so that the EPR line typically narrows as T_c is approached. In $NiCl_2$, since the in-plane coupling is both ferromagnetic and much stronger than the antiferromagnetic between-plane interaction, one would expect the fluctuations to be predominantly ferromagnetic and two dimensional outside of the critical region. This contrasts with the behavior

very near T_N, where it is known from direct quasielastic-neutron-scattering measurements[3] that $\chi(\vec{q})$ is relatively isotropic in $\vec{q}$. Thus the decrease of $\Delta H_{\parallel,\perp}$ down to 70 K and the subsequent divergence indicates a changeover from ferromagnetism to antiferromagnetism, which in this case involves a crossover from two- to three-dimensional fluctuation behavior.

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Note added.—Since this work was submitted for publication, K. Kawasaki has pointed out to us that he has developed an alternative theory, discussed briefly in Phys. Lett. 26A, 543 (1968), which predicts $1/T_2 \sim \tau^{-9/2\nu+2-2\alpha}$, valid for both $\alpha > 0$ and < 0. With the use of current values for the Heisenberg model, $\nu \sim \frac{2}{3}$, $\alpha \sim -\frac{1}{8}$, this gives an exponent of $-\frac{3}{4}$, in excellent agreement with our experimental value -0.7 ± 0.1. Full details of this theory have not yet been published, so it is not possible to consider its applicability to $NiCl_2$ in detail.

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[5]M. P. Schulhof, P. Heller, R. Nathans, and A. Linz, Phys. Rev. B 1, 2304 (1970). The EPR in MnF_2 above T_N has been studied in detail by M. S. Seehra and T. G. Castner, Solid State Commun. 8, 787 (1970); and by M. S. Seehra, J. Appl. Phys. 42, 1290 (1971), and Phys. Rev. B 6, 3186 (1972). They find that for $0.03 < \tau \lesssim 1$ the temperature-dependent part of ΔH diverges like $\tau^{-1.2}$. Below $\tau \sim 0.03$ the EPR line becomes asymmetric and the linewidth markedly field dependent, so it is not possible to define a critical exponent in this region. As noted in the text, the RPA theory is only expected to be valid for $\tau \gtrsim 0.04$ in MnF_2. Thus the exponent -1.2 seems to be characteristic mainly of the *precritical region* in MnF_2. It should be noted, however, that Seehra does observe the $1 - \frac{1}{2}\sin^2\theta$ angular dependence for $\tau < 0.15$, in agreement with our results in $NiCl_2$.

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Mass Discrepancy in the Iron Region*

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We have found an indication of systematic discrepancies in the tabulated mass values in the iron region. We have measured the Q value for $^{58}Ni(p,\alpha)^{55}Co$ and found it to be -1.3410 ± 0.0029 MeV. This differs by 17.3 keV from the value of -1.3583 ± 0.0045 MeV calculated from the 1971 mass tables.

In the 1971 compilation of atomic masses,[1] the comment appears on page 365, "Even after multiplying the errors by 1.5, the new results for ^{57}Fe differ by 3 errors from older results. The earlier mass doublets in this whole region are connected in a satisfactory way by dependable reaction energy values. Unless the new value itself is in error by as much as about 27 keV, this would mean that these earlier values contain a rather large systematic error." We have just found a discrepancy in the ^{58}Ni-^{55}Co mass difference which suggests that there may well be rather large errors in the compilation values in this mass region. During the course of our measurement[2] of accurate excitation energies in ^{55}Co we noted differences of almost 20 keV in the Q value for $^{58}Ni(p,\alpha)^{55}Co$ from that calculated from the masses given in the 1971 table even though the stated uncertainties for ^{58}Ni and ^{55}Co were 3.1 and 3.3 keV, respectively. In order to resolve this apparent discrepancy we have made an accurate measurement of the ground-state Q