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Critical behavior of the electron-paramagnetic-resonance linewidth of a spin-$\frac{1}{2}$ two-dimensional antiferromagnet

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The 9-GHz data on the electron-paramagentic-resonance linewidth of a two-dimensional spin-$\frac{1}{2}$ antiferromagnet [$Cu(HCOO)_2 \cdot 4H_2O$] have been reanalyzed just above the Néel temperature T_N. The temperature dependence of the critical broadening contribution observed between $2T_N$ and $1.5T_N$ [$T_N = 17$ K] is exponential in $1/T$ with an isotropic characteristic energy and is in very good agreement with the ξ^3 dependence (ξ=spin-correlation length) predicted by theory. The data suggest the critical spin fluctuations depend only on a single parameter, the spin-stiffness constant.

The study of quantum fluctuations of two-dimensional (2D) spin-$\frac{1}{2}$ quantum antiferromagnets has been significantly revived with the discovery of the high-temperature cuprate superconductors. There have been numerous experimental and theoretical studies of these systems in the last several years with recent reviews of this subject by Manousakis[1] and Birgeneau.[2] Although neutron-scattering results[3] for La_2CuO_4 have yielded the temperature dependence of the spin-correlation length in agreement with theoretical predictions[4,5] of an exponential temperature dependence for this length, efforts by experimentalists[6–8] to observe the critical behavior of the electron-paramagnetic-resonance (EPR) linewidth associated with the planar 2D antiferromagnetically coupled lattice of Cu^{2+} ions have been unsuccessful. Although EPR signals from Cu^{2+} have been observed due to nonsuperconducting phases, the failure to observe the signal due to the Cu^{2+} ions in the cuprate planes has been attributed[6,9] to the strong dependence of the EPR linewidth on the correlation length and the large Heisenberg exchange, resulting in very large spin-correlation lengths at temperatures just above the Néel temperature ($T_N > 300$ K for La_2CuO_4). Chakravarty and Orbach[9] (CO), and more recently Lazuta,[10] have calculated the temperature dependence of the EPR linewidth for the 2D S-$\frac{1}{2}$ case. The CO calculation for La_2CuO_4 yields a width of 100 kG at 400 K and 13 kG at 500 K, thus offering one explanation why experimental attempts[6] up to 600 K to observe the planar Cu^{2+} signal have been unsuccessful. However, there are other 2D S-$\frac{1}{2}$ copper salts that were studied more than two decades ago. One of these, copper formate tetrahydrate [$Cu(HCOO)_2 \cdot 4H_2O$)], exhibits a Heisenberg exchange interaction between planar Cu^{2+} ions of order 100 K and a Néel temperature of 17 K. We studied[11] the temperature dependence of the EPR linewidth between 24 and 300 K. It exhibited a linear temperature dependence of the linewidth between $2T_N$ and $20T_N$ which was explained[11,12] by phonon modulation of the Dzialoshinsky-Moriya (DM) interaction. Although critical EPR linewidth broadening was reported in this work, no detailed analysis of the data between $1.5T_N$ and $2T_N$ was done because of a lack of relevant, plausible theoretical predictions at that time. Below we reanalyze the critical behavior of the EPR linewidth approaching T_N and compare it with the theory.[9,10] These results give experimental evidence supporting the theory and further elucidate the difficulty of obtaining similar EPR results for the cuprates.

$Cu(HCOO)_2 \cdot 4H_2O$, which was first suggested as a 2D antiferromagnet by Martin and Waterman,[13] has a lower symmetry (monoclinic, $P2_1/a$, with $a = 8.18$ Å, $b = 8.15$ Å, and $c = 6.35$ Å) than the cuprates and the two Cu^{2+} ions in the unit cell are inequivalent with different g tensors. This latter feature leads to exchange broadening[14] of the EPR linewidth at larger magnetic fields. The individual formate ions [$(HCOO)^-$] are actually tilted out of the a-b plane in a complex manner leading to more components of the DM antisymmetric exchange vector than in the cuprates. It has been demonstrated[12] that the DM interaction makes the dominant contribution to the second moment and to the magnitude of the exchange-narrowed EPR linewidth well above T_N. Although the individual components of the DM vector for copper formate have not been determined an estimate of the DM exchange interaction has been determined from the antiferromagnetic resonance (AFMR) experimental results.[15] The theories of the critical spin fluctuations for the 2D S-$\frac{1}{2}$ case depend solely on the Heisenberg exchange J and the temperature. An early estimate[16] of $J \simeq 71.5$ K for $Cu(HCOO)_2 \cdot 4H_2O$ came from the susceptibility maximum near 65 K and a comparison with the high-temperature series expansion formula for the 2D S-$\frac{1}{2}$ case. More recently larger values of J have been determined from neutron-scattering results[17] on deuterated copper formate [$Cu(DCOO)_2 \cdot 4D_2O$], which have yielded values of J of 89 K from the temperature dependence of the spin-correlation length and 108 K [9.3 ± 0.1 meV] from the spin-wave dispersion curve. We suggest this latter value of J to be the most accurate value determined to date for the copper formate system.

The EPR measurements were made at both 9 and 36 GHz in a temperature range from just above T_N to 300 K. Only the 9-GHz results in the temperature range 24 to 44 K will be considered here. In the AF phase there is a field of order 5.3 kG above which the equilibrium orientation of the spin sublattices is altered from that in the low-field regime. At 9 GHz the exchange broadening contribution to the EPR linewidth is negligible ($<3\%$) and the critical behavior of the EPR linewidth should be very close to that expected at very small fields. In Fig. 1 the EPR linewidth is shown versus temperature for the magnetic field along the directions L_1, L_2, and L_3 [L_2 lies along the *b* axis, L_3 is close to the *a* axis in the *ab* plane, and L_1 is perpendicular to the *ab* plane]. The linewidth shows a minimum at 34, 35, and 32.5 K for L_1, L_2, and L_3, respectively. At 36 GHz the minimum linewidth temperature shows considerably more anisotropy. Above the minimum the linewidth shows the slow linear increase with temperature that has been discussed in Refs. 11 and 12. The rapid increase in the linewidth below the minimum results from the critical spin fluctuations and is observed readily between $2T_N$ and $1.5T_N$. The linewidth for the field along L_2 continued to broaden below $1.5T_N$, but the line shape became asymmetrical and the linewidth analysis became less certain. To obtain the extra linewidth due to critical behavior the slowly varying portion of the form $\alpha+\beta T$ was subtracted from the total linewidth. The values of α and β for the L_1, L_2, and L_3 directions are given in Table I. In Ref. 11 the slope of the linear temperature dependence was determined from data above 70 K which led to different values of α and β than those employed here. Practically, the critical broadening portion of the linewidth from the data in Ref. 11 is too small to be determined as the temperature approaches the value where the linewidth is a minimum and the smallest reliable values of excess linewidth obtainable are of order 2 Oe. The excess or critical linewidth broadening versus T_N/T is shown in Fig. 2. Despite some scatter in the data the overall dependence of the critical linewidth is best fit by an exponential temperature dependence for $1.5<T/T_N<1.9$. For the L_2 field direction the data extends over nearly two decades in linewidth for a temperature range of only 8 K. The somewhat weaker signals for the L_1 and L_3 directions permitted observation of the critical broadening over a smaller temperature range, however, the exponential temperature dependence is qualitatively and quantitatively very similar to that for the L_2 direction. The slopes [W, $\Delta H_c \propto \exp(W/T)$] for the three directions are also given in Table I. The magnitude of the critical broadening for the L_3 direction is a factor of 3 smaller than that for L_2, but the temperature dependence is nearly the same. This linewidth anisotropy is similar to that observed in susceptibility data.[18] The susceptibility anisotropy was explained in terms of the weak ferromagnetic moment lying in the L_1-L_2 plane. All components of the EPR linewidth (the α, the βT, and the critical behavior) show a smaller magnitude for the field along L_3. This is consistent with the largest component of the DM interaction being along L_3 which is consistent with the weak momentum lying in the L_1-L_2 plane. In Ref. 11 the

TABLE I. Experimental linewidth parameters.

Field direction	α (Oe)	β (Oe/K)	W (K)
L_1	9(2)	1.1(8)	4(03)
L_2	16(6)	1.0(5)	40(8)
L_3	3(5)	1.0(0)	4(21)

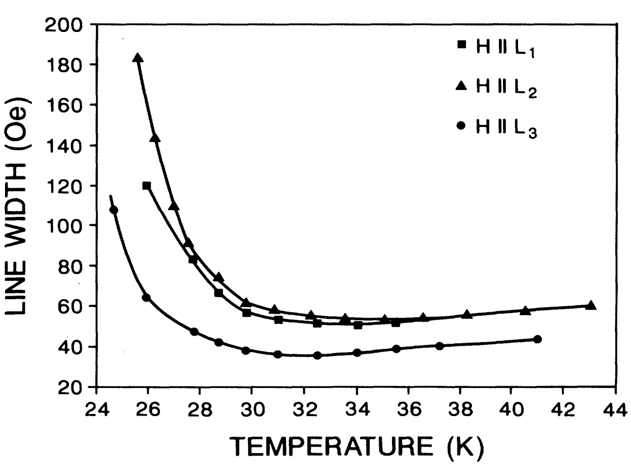

FIG. 1. The 9 GHz EPR linewidth results for $Cu(HCOO)_2$ $4H_2O$ for three mutually orthogonal field directions. L_2 lies along *b* axis, L_3 is close to the *a* axis in the *ab* plane, while L_1 is perpendicular to the *ab* plane.

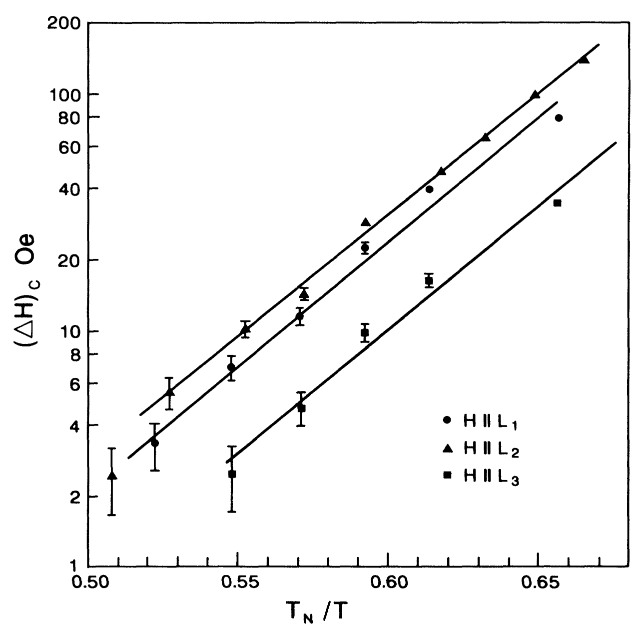

FIG. 2. The critical contribution of the 9 GHz EPR linewidth vs T_N/T for the three orthogonal field directions. Within experimental error [less than 1 Oe] the slopes of $\ln(\Delta H)_c$ vs $1/T$ are the same for the three field directions. The slopes (characteristic temperatures) are given in Table I.

critical linewidth was compared with Mori's theoretical prediction[19] that $\Delta H_c \propto 1/(T-T_N)^n$, but the values of n obtained were considerably larger than expected from the theory. The apparent exponential behavior of the critical broadening with temperature suggests a comparison with the CO (Ref. 9) and Lazuta[10] predictions.

The temperature dependence of ΔH_c is given by[9,10]

$$\Delta H_c\langle T\rangle = B\frac{\omega_p^2}{\omega_{\rm ex}}\left[\frac{\xi}{a}\right]^3 \frac{(T/2\pi\rho_s)^{5/2}}{(1+T/2\pi\rho_s)^4}, \tag{1}$$

where ω_p^2 is the second moment M_2, $\omega_{\rm ex}$ is the Heisenberg exchange frequency, ρ_s is the spin-stiffness constant, and ξ/a is the ratio of the temperature-dependent spin-correlation length to the spin-spin nearest-neighbor distance, which is given as

$$\frac{\xi}{a} = C_\xi \frac{\exp(2\pi\rho_s/T)}{(1+T/2\pi\rho_s)}. \tag{2}$$

The constant B in (1) contains renormalization factors and is the order of unity, but is not relevant for consideration of the temperature dependence of the EPR linewidth. Similarly, the constant prefactor (2) only affects the magnitude of ΔH_c. Chakravarty, Halperin, and Nelson[5] have found a pure exponential dependence without the factor in the denominator in a two loop approximation, whereas the one loop approximation yields a $1/T$ prefactor. It is important to note that the critical broadening is only a function of $2\pi\rho_s/T$ and that $\rho_s = kJ$ where k is a constant in the range of 0.15 to 0.25 depending on the theory. We will employ $k=0.18$ as found by Singh and Huse[20] and also in Ref. 4, however it is worth noting that values in the 0.20 to 0.22 range have been obtained in Monte Carlo calculations.[21] In essence a single parameter J determines the temperature dependence of the EPR linewidth critical broadening. Despite differing values of J from earlier studies J is now well enough established[17] to warrant comparing the calculated results from (1) with the data.

Figure 3 shows calculated curves using $J=108$ K and $k=0.18$ and the CO expression in Eq. (1). Also shown are curves showing $\Delta H_c \propto (\xi/a)$, $(\xi/a)^2$, and $(\xi/a)^3$ based on Eq. (2). The linear dependence on (ξ/a) has been considered earlier by Mehran and Anderson[6]. It is much too slow a temperature dependence to explain the data. The cubed dependence on (ξ/a) is in good agreement with the observed data for the L_2 field direction. The CO expression yields a result that is intermediate between the $(\xi/a)^2$ and $(\xi/a)^3$ expressions for ΔH_c. The CO expression yields nearly the right slope for $T_N/T=0.66$, but the slope and temperature dependence is only one-half of the data at $T_N/T=0.5$. What is particularly striking about the data is how closely ΔH_c seems to obey an exponential law in $1/T$. The nonexponential denominator in ξ/a in Eq. (2) is too small to distinguish from the pure exponential in $1/T$, however, the $(T/2\pi\rho_s)^{5/2}$ term in Eq. (1) leads to some nonexponential behavior not consistent with the data. One is forced to conclude that the data for ΔH_c are varying somewhat more rapidly with temperature than the CO expression for the parameters chosen.

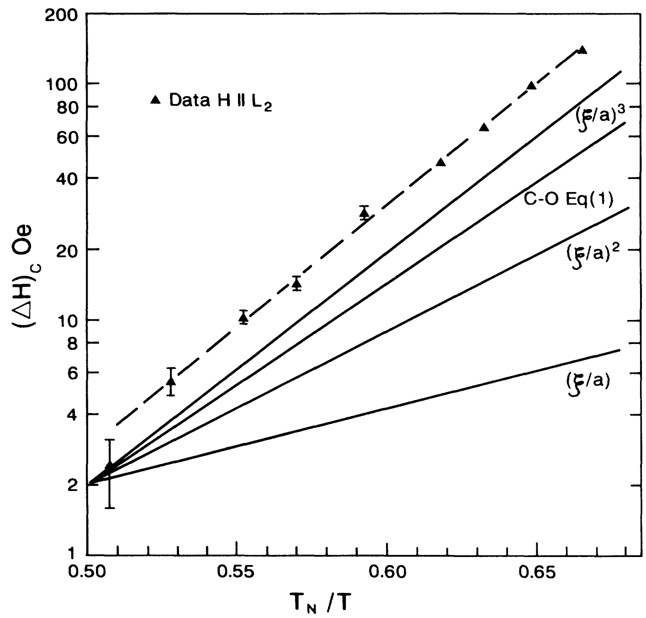

FIG. 3. Calculated expressions for $(\Delta H)_c$ dependence on $(\xi/a)^n$ [$n=1$, 2, and 3] and the Chakravarty-Orbach expression in Eq. (1) vs T_N/T for $J=108$ K and $k=0.18$ are compared with the data for the L_2 field direction. ξ/a has been calculated with Eq. (2). The calculated curves have been arbitrarily normalized to a value of 2 Oe at $T_N/T=0.50$. The CO expression exhibits more curvature than the pure $(\xi/a)^n$ terms because of the $T^{5/2}$ term in Eq. (1).

Chakravarty and Orbach noted that Birgeneau suggested the $(\xi/a)^3$ dependence of ΔH_c for the 2D case on general grounds. If one adopts the viewpoint that ΔH_c must be proportional to $(\xi/a)^3 f(T)$ as in Eq. (1), that (ξ/a) is purely exponential in $1/T$, and that there is no other contribution [$f(T)=$constant] to the temperature dependence of ΔH_c then one can force fit the temperature-dependent data to a constant times $(\xi/a)^3$ and obtain empirical values of ρ_s (and J if k is given). This leads to a value of ρ_s of 21.(6) K, which is a factor 1.6 larger than that found by neutron scattering[17] for the deuterated copper formate. This might imply that not all of the temperature dependence of ΔH_c is coming from $(\xi/a)^3$ and that $f(T)$ is increasing as T is decreased toward T_N. However, the $f(T)$ in Eq. (1) has the wrong temperature dependence and actually decreases by a factor of 2 between $2T_N$ and $1.5T_N$. Using $k=0.18$ we obtain values of J equal 1(19), 12(0), and 1(24) K, respectively for the L_1, L_2, and L_3 axes from this forced fit. These values average 12% higher than the 108 K used for the calculated curves based on the spin-wave dispersion results.[17] Alternatively, fitting the L_2 data with ξ/a given by Eq. (2) reduces ρ_s and J by 7% to 20.2 and 112 K, respectively. The data is certainly consistent with a $(\xi/a)^3$ dependence of ΔH_c. A small nonexponential contribution to ΔH_c in $1/T$ cannot be established from the present data.

The magnitude of the critical broadening is also of interest. For the L_2 direction $(\omega_p^2/\omega_{ex}) \sim 16.6$ Oe, $B = 3.0$, $\xi/a = 49.3$ (for $C_\xi = 0.5$), and $f(T) = 0.0094$ at $T_N/T = 0.66$ one obtains a value of $\Delta H_c \sim 1120$ Oe, a factor of 8 larger than the experimental value in Fig. 2. The present theories[9,10] for the cuprate differ on the origin of the anisotropic exchange contributing to ω_p^2 in Eq. (1). CO employ the much larger antisymmetric anisotropic exchange (DM interaction), while Lazuta claims only the symmetric anisotropic exchange contributes to the ξ^3 portion of $\Delta H_c(T)$ for the La_2CuO_4 case (one component of the DM interaction along the a axis). The low monoclinic symmetry and the more complex superexchange via the formate ion for $Cu(HCOO)_2 \cdot 4H_2O$ suggest a more complex anisotropic exchange for this case than for the cuprate. Our AFMR results[15] show the symmetric anisotropic exchange would lead to a value of ω_p^2 2 orders of magnitude smaller than that from the DM interaction, which is more than a factor of 10 too small to explain the experimental result. Understanding the magnitude and anisotropy of $\Delta H_c(T)$ for $Cu(HCOO)_2 \cdot 4H_2O$ requires additional work.

A comparison of $Cu(HCOO)_2 \cdot 4H_2O$ with La_2CuO_4 shows that they have roughly comparable values of T_N/J, but the Heisenberg exchange and the DM interaction are at least an order of magnitude larger for the cuprate leading to the prefactor ω_p^2/ω_{ex} in Eq. (1) being an order of magnitude larger or more for the cuprate. The most important factor seems to be the high temperature required to obtain a sufficiently small value of ξ/a in addition to the larger value of ω_p^2/ω_{ex}, making it difficult or impossible to observe the planar Cu^{2+} EPR signal in the cuprate. Our results show that a minimum in the total EPR linewidth is found at $T/T_N \sim 2$. If this were to carry over to La_2CuO_4 one would expect the minimum EPR linewidth to occur in the 600–660 K range, but measurements[7] to 600 K on La_2CuO_4 have already been unsuccessful, thus making clear the problems in obtaining EPR results for the planar Cu^+ in the cuprates.

In summary the EPR linewidth data for $Cu(HCOO)_2 \cdot 4H_2O$ in the critical regime is shown to vary exponentially with $1/T$ for all three mutually orthogonal field directions with virtually no anisotropy in the characteristic temperature. The data is certainly consistent with the ξ^3 dependence suggested by Birgeneau and calculated by theory, although uncertainties in the constant k relating the spin-stiffness constant ρ_s and the Heisenberg exchange J in this temperature range make it difficult to establish whether nonexponential terms beside that resulting from the ξ^3 temperature dependence contribute to the EPR linewidth. The observed critical broadening is consistent with the theoretical prediction that critical spin fluctuations for a 2D S-$\frac{1}{2}$ antiferromagnet depend only on a single parameter, namely, ρ_s or J. The magnitude of the critical linewidth is not yet understood.

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