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Electron paramagnetic resonance of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$

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The electron paramagnetic resonance of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ has been studied in the temperature range of 4 K to room temperature. This compound is known to behave magnetically as a spin-$\frac{1}{2}$, one-dimensional Heisenberg ferromagnetic with ordering below 1K. In the high-temperature regime the EPR data show a rich angular dependence of the linewidths as the magnetic field is rotated away from the chain. The data were analyzed in manner similar to that used by McGregor and Soos, who used the Blume-Hubbard result for spin dynamics and extracted exchange anisotropies in one dimension. For adequate fit, we reduced the symmetry of symmetric anisotropic exchange to orthorhombic and included the antisymmetric exchange. Isotropic symmetric, dipolar, anisotropic symmetric, and antisymmetric exchange therefore were included with the room-temperature results of $J_0=0.8$ K, $D_d=0.058$ K, $D_e=0.032$ K, and $d=0.043$ K, respectively, and further show about a 12% XY character to the exchange. These results are reasonably consistent with the previous results on this compound. Splitting of the EPR lines indicate that there are two inequivalent chains along the needle axis. Data to 4 K indicate no significant changes in the angle dependence but an anomalous monotonic broadening of the linewidths is observed as temperature is lowered.

I. INTRODUCTION

The structural studies[1] of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ (TMACuC) indicate a rather well-isolated, double chlorine-bridged chain of Cu^{2+} ions coupled by H_2O and Cl^- to neighbor chains, with the TMA cations in the third spacial direction. Recent magnetic- and specific-heat studies[1,2] indicate that TMACuC is an example of a very weak one-dimensional, spin-$\frac{1}{2}$ Heisenberg ferromagnet, a system which is currently of considerable interest. Early magnetic susceptibility measurements of Stirrat *et al.*[3] indicated a fit that suggested a layered structure with $J=0.28$ K and a transition temperature of $T_c=0.157$ K. They also measured the EPR linewidths but did not report their angular dependence. Losee *et al.*[1] have given the exchange along the chain to be less than 1 K, which was refined by Algra *et al.*[2] to 0.85 K. This latter work showed that exchange in the chain direction is significantly greater than perpendicular to it, clearly indicating the one-dimensional (1D) character of the magnetic behavior. That work also estimated the exchange anisotropy to be about 10% of the isotropic exchange and gave the transition temperature to be $T=0.165$ K. More generally there has been recent work related to the EPR of the linear-chain copper complexes,[4–6] which shows that EPR linewidth studies can provide additional detailed information concerning the interaction between localized spins. In particular it was shown that the symmetric anisotropic exchange and the dipolar interactions can be determined by analyzing the angle dependence of the EPR linewidths.

In this paper we present the EPR linewidths as a function of sample orientation. These data are analyzed by adopting the procedure followed by McGregor and Soos who calculated the width of the EPR line by using general linewidth theory,[7] and then specializing by including the Blume-Hubbard[8] result for spin dynamics and preferentially weighting the anisotropic (ae) and dipolar (dip) terms in one dimension. Their work emphasizes the effects of spin correlation on the local perturbing fields (ae and dip) and assumes that the symmetric exchange J_0 is significantly greater than the Larmor energy $g\mu_B H_0$. In TMACuC the symmetric exchange is weak, but nevertheless it is sufficient to slightly narrow the dipolar broadened lines and to give moderately good agreement with theory with respect to the angular dependence of the linewidths. Finally, we have included the antisymmetric contribution to the exchange, which is likely present owing to the low symmetry of the local spin site in TMACuC.

II. CRYSTAL STRUCTURE

Various conventions have been followed in the assignment of axes to the crystal structure of TMACuC. Groth first examined the system morphologically,[9] but both Losee *et al.*,[1] and later Algra *et al.*,[2] have studied TMACuC relative to the crystallographic unit cell and have switched Groth's a and c axes and defined the c' axis in the $\vec{a}\times\vec{b}$ direction. Finally, Algra *et al.*[2] define x,y,z axes when referring to exchange directions where x and y correspond to a and b, while z corresponds to $\vec{a}\times\vec{b}$, the reciprocal axial direction.

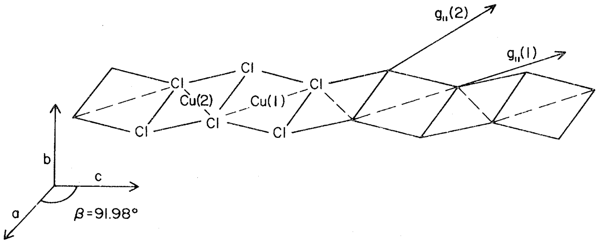

FIG. 1. Cu-Cl-Cu chain in $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ relative to Groth's morphological axes. *c* axis is the chain direction and *a* axis is the shortest morphological direction; the direction of the $(CH_3)_3NH$ cation van der Waals bonding.

Since in this work the crystals were oriented using the external morphology, it was convenient to use the axes of Groth. These were related to the other systems as described above. The structure as determined by Losee *et al.* consists of chains of copper atoms linked by pairs of chloride bridges where the bridge distances are very different because of the strong tetragonal distortion of the copper coordination sphere. The remaining two coordination positions of the distorted octahedral sphere are filled by water molecules. A diagram of this chain is shown in Fig. 1. These chains are linked into weakly bound layers by hydrogen bonding between the coordinated water molecules and an isolated (uncoordinated) chloride ion. The layers so formed are separated from each other by the TMA cations, the only obvious binding forces being that of van der Waals. One can thus speak of a chain direction, a hydrogen-bonding direction, and a van der Waals direction. These correspond to Groth's *c*, *b*, and *a* axes, respectively. The crystals grow as needles along the *c* direction. Sometimes, but not always, they are also lamellar: When this habit occurs the smallest dimension of the crystal corresponds to *a*.

In terms of Groth's morphologic axes, the space group of the system is $P2_1/a$, and the cell dimensions are $a=16.730(23)$ Å, $b=7864(11)$ Å, $c=7.479(10)$ Å, and $\beta=91.98(3)°$. The only difference between these values and those reported by Losee *et al.* is that *a* and *c* have been interchanged. Table I lists the correspondence between various axes that have been previously used in the literature.

One feature of this structure has not been mentioned in the literature and is important to the interpretation of the EPR spectrum. Within each chain two crystallographically inequivalent copper atoms alternate, and their coordination orientations differ. As will be noted later, the system has been treated as a simple tetragonal distortion of a regular octahedral sphere. The tetragonal axes of the inequivalent sites are not exactly parallel. Both of them lie approximately along the [101] direction of the lattice, but with respect to the plane of the hydrogen-bonding interaction (*a*-*c*) they subtend rather different angles. The copper (1) sphere is canted at an angle of 13° with respect to this plane, while copper (2) is canted by only 0.75°.

TABLE I. Correspondence between various axes previously used in the literature.

	Losee *et al.*	Algra *et al.*	Groth
Chain direction	a_0	x	c
Hydrogen-bond direction	b_0	y	b
van der Waals direction	c_0 $c^*(a_0 x b_0)$	Z	a

In the chains adjacent along *b*, the hydrogen-bonding direction, all copper coordination spheres are similarly canted in the same direction. These adjacent chains are related to the index one by a screw axis and a twofold axis. In the neighboring planes, related to the index chain by a glide, all of the coordination planes tilt slightly in the opposite direction. Thus within each chain there are two orientations of the copper coordination sphere, canted in the same direction by different angles; within each plane of the H-bonded chains all coordination spheres are canted the same way, and in adjacent planes, the coordination spheres cant the opposite way. The two orientations in alternate planes are distinguishable and can be seen in this work. The two orientations within each chain are exchange coupled and not distinguishable; an average orientation has been seen which corresponds closely to the calculated average of the two orientations.

It is possible that a third interplane superexchange mechanism exists along the Cu-Cl-(CH_3)NH-Cl-Cu pathway, but present data do not unequivocally show it. Algra *et al.*[2] have estimated the exchange ratio J_c:J_b:J_a (J_x:J_y:J_z in their notation) as 1:0.05:0.015 indicating a quasi-1D exchange interaction in TMACuC.

III. EPR DATA

EPR spectra were taken in the temperature range 4—330 K with a Varian E-109 series *X*-band microwave spectrometer. Temperatures less than 77 K were obtained with an Oxford Instruments flow-through cryostat, and those greater than 77 K by a Varian temperature-control unit. The *K*-band data were taken on a standard homodyne spectrometer with a variable-temperature cavity in a helium bath.[10] Crystals were rejected on the basis of three criteria: (1) twinning, (2) occluded solution within the crystal, and (3) crystal age. The latter criterion proved important since the crystals slowly decompose at room temperature.

A single EPR resonance is obtained for the *a*-*c* plane rotation, but resolvable splitting owing to the two inequivalent Cu^{2+} sites occurs for *b*-*c* and *a*-*b* plane rotation. This behavior is shown for all three rotation planes in Fig. 2. At $T=300$ K and at the *X* band all observed peak-to-peak linewidths ΔH_{pp} were less than 120 G, while the maximum linewidth *increased* to 180 G at 4 K. The lines are slightly broader with a greater angle dependence at *K* band. The angle dependence of ΔH_{pp} for *a*-*c* rotation is shown in Fig. 3.

The elements of the *g* tensor were obtained by standard methods from measurements of the *g*-value variation in the *a*-*b*, *a*-c^*, and *b*-c^* planes. Since TMACuC is monoclinic, the c^* is the axis defined to be perpendicular to the *a*-*b* plane and differs by less than two degrees from the *c*

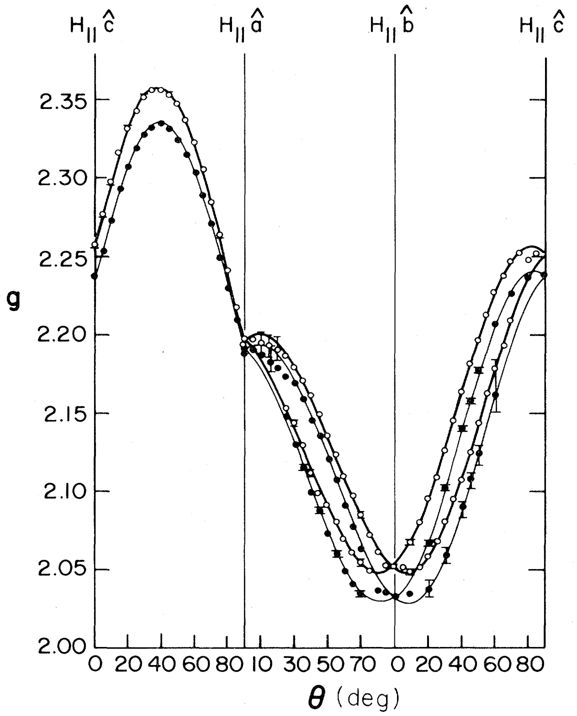

FIG. 2. g vs θ about each of the morphological axes. Slightly inequivalent chains give rise to the splitting. No noticeable splitting occurs for a-c plane rotation. Open circles are room-temperature data and the solid circles are at 100 K.

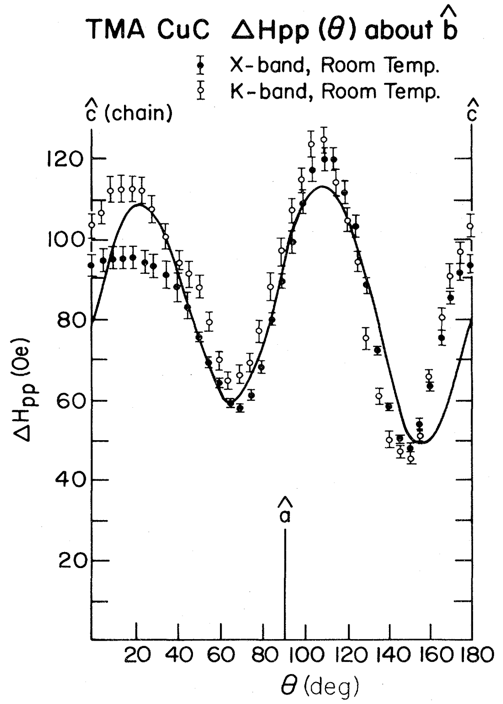

FIG. 3. Angular dependence of the linewidth for a 180° rotation in the a-c plane. Best fit is shown as the solid line. Open circles are K-band data and closed are data at the X band.

TABLE II. Principal axes of the g tensor for the two inequivalent sites in TMACuC. θ is measured from c. ϕ is measured from a about c. (See Fig. 4.)

		θ	ϕ
		Tensor 1 Room temperature	
g_{ZZ}	2.356	38.6°	−1.8°
g_{YY}	2.108	58.9°	141.0°
g_{XX}	2.028	110.4°	64.0°
		Tensor 2	
g_{ZZ}	2.356	38.6°	1.92°
g_{YY}	2.108	59.0°	141.0°
g_{XX}	2.028	110.5°	63.9°
		Tensor 1 100 K	
g_{ZZ}	2.333	40.0°	−1.7°
g_{YY}	2.103	56.3°	144.3°
g_{XY}	2.014	108.9°	67.6°
		Tensor 2	
g_{ZZ}	2.333	40.1°	0.6°
g_{YY}	2.099	55.3°	145.8°
g_{XX}	2.017	107.6°	68.5°

axis. The principal g values associated with each site are given in Table II.

IV. ANALYSIS

The spin Hamiltonian for the system may be written

$$H = H_z + H_{\mathrm{ex}} + H_{\mathrm{dip}} + H_{\mathrm{ae}} + H_{\mathrm{DM}} , \tag{1}$$

where $H_z = \mu_B \sum \vec{\mathrm{H}}_0 \cdot \vec{\mathrm{g}} \cdot \vec{\mathrm{S}}_n$ is the Zeeman interaction, $H_{\mathrm{ex}} = 2J_0 \sum \vec{\mathrm{S}}_n \cdot \vec{\mathrm{S}}_{n+1}$ is the usual symmetric exchange interaction, $H_{\mathrm{dip}} = \sum_{\rightarrow} \vec{\mathrm{S}}_n \cdot \vec{\mathrm{D}}_d \cdot \vec{\mathrm{S}}_{n+1}$ is the dipolar interaction, $H_{\mathrm{ae}} = \sum \vec{\mathrm{S}}_n \cdot \vec{\mathrm{D}}_e \cdot \vec{\mathrm{S}}_{n+1}$ is the symmetric anisotropic exchange interaction, and $H_{\mathrm{DM}} = \sum \vec{\mathrm{d}} \cdot \vec{\mathrm{S}}_n x \vec{\mathrm{S}}_{n+1}$ is the Dzyaloshinksi-Moriya antisymmetric exchange,[11,12] often referred to as the $S \times S$ interaction. While H_{dip} is summed over many neighbors, H_{ex}, H_{ae}, and H_{DM} are summed over nearest neighbors only. Since the nearest-neighbor Cu^{2+} ions are less than 5 Å apart, hyperfine interactions may be neglected.

Because of the weak exchange in this system, spin-diffusive effects are minimized so our analysis will follow the approach of McGregor and Soos (MS).[4] For a-c plane rotation, an average g tensor is defined in accordance with the single EPR lines observed. To simplify the calculations, it is noted that the principal g values are axially symmetric to within 3%. This allows one to define $g_{\parallel} = g_Z$ as the average of g_{ZZ} on both sites, i.e., both chains, and $g_{\perp}$ as the average of both g_{XX} and g_{YY} for both sites, where X, Y, and Z are the axes of the principal g tensor. To simplify the calculation we assume that all Cu^{2+} sites on the same chain are magnetically equivalent. To compare theory and experiment, all relevant angles are ex-

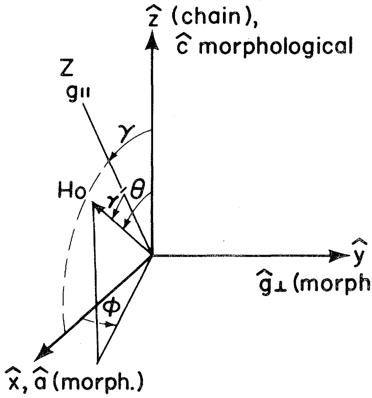

FIG. 4. Coordinate system used in theoretical treatment of the various interactions. Z axis is defined along the direction of strong exchange (the chain axis) and H_0 represents the direction of the applied magnetic field.

pressed with respect to coordinates used by MS which defines z to be along the linear chain, and y to lie within the plane of axial symmetry of the averaged g^{XYZ} tensor. In the case of TMACuC, y corresponds to Y, and at room temperature Z ($g_{\|}$) lies 38.6° from the z (chain) axis, as shown in Fig. 4.

The linewidths as a function of angle can be found by calculating the secular and nonsecular parts of the second moment. The approach of MS assumes axial symmetry for the anisotropic exchange from which the second-moment expressions can be written: These are Eqs. (19) and (20) of MS. Applying these to TMACuC, we find qualitative agreement, however, a considerably better fit is obtained by reducing the symmetry of the anisotropic exchange term from tetragonal to orthorhombic. An explicit expression for H_{ae} then becomes

$$D_e^{\text{mol}} \equiv \frac{D_e}{3} \begin{bmatrix} q & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & 2 \end{bmatrix} ,$$

where we have chosen $q=-1-\Delta$ and $p=-1+\Delta$ in order to maintain a zero trace operator, and the principal axes are those of the averaged g tensor. Transforming to the laboratory coordinates then involves a rotation of D_e^{mol} about Z by an angle α, and a rotation about y by the γ'. An interesting feature here is that the purely secular part of the anisotropic exchange does not depend on α, that is, it does not depend on the rotation of the distortion about Z.

In these coordinates, and for nearest-neighbor interactions only, the nonsecular contribution of $H_{\text{dip}}+H_{\text{ae}}$, to the second moment is found to be

$$M_2 = \frac{3S(S+1)}{2h^2} \left[\frac{1}{3} \left(\frac{D_e}{3} \right)^2 [(3-2\Delta)\cos^2\gamma' + (3+2\Delta)] + D_d^2(\cos^2\theta + 1) - \frac{D_e D_d}{3} \{ [(3+\Delta)\cos^2\gamma' - (1+\Delta)](3\cos^2\theta - 1) + \tfrac{1}{3}[-2\Delta + (3+\Delta)\sin^2\gamma']\sin^2\theta\cos[2(\alpha+\phi)] \} \right] , \tag{2}$$

where $D_d=(\bar{g}\beta)^2/r^3$, $\bar{g}^2=(2g_{\perp}^2+g_{\|}^2)/3$, and r is the nearest-neighbor distance. Similarly the secular contribution is

$$M_2'(0) = \frac{3S(S+1)}{2h^2} \left[\frac{D_e}{3}[(3+\Delta)\cos^2\gamma' - (1+\Delta)] - D_d(3\cos^2\theta - 1) \right] . \tag{3}$$

Note that for $\Delta=0$ these equations reduce to Eqs. (19) and (20) of MS, respectively.

In an earlier work on copper (II) complexes,[13] it was found that the g anisotropy could be approximated by defining an effective spin quantization axis $\vec{g}\cdot\vec{H}_0$, where g is an averaged g^{XYZ} calculated from Table II. This results in effective angles θ_{eff}, ϕ_{eff}, and δ_{eff} which have been substituted for their counterparts in Eqs. (2) and (3).

We have also described the $S \times S$ interaction in the coordinates of Fig. 4. The only symmetry elements within the chain are centers of symmetry at each copper atom. Hence, according to the symmetry rules of Moriya,[11] $\vec{d}$ lies completely within the a-c plane and near the a axis. For a-c plane rotation this results in a contribution to the second moment of the form[13]

$$M_2^A = (d^2/8)[2 + \sin^2(\theta - \theta_A)] , \tag{4}$$

where d is the scalar magnitude of the $S \times S$ interaction.

Neglecting next-nearest neighbors and hyperfine interactions the relationship between calculated and observed linewidths is expressed as

$$(\tfrac{3}{2})\Delta H_{\text{pp}} = [\sqrt{2}/(3J_0)][M_2' + \rho M_2'(0) + M_2^A] . \tag{5}$$

The adjustable parameters in this equation are the magnitudes of J_0, D_e, Δ, d, and θ_A. The semipositive parameter ρ enhances the secular spin interaction, that is, when $\rho=0$, secular and nonsecular contributions to M_2 are equally weighted, while for $\rho>0$, the secular components are preferentially weighted. At X band the isotropic exchange energy in TMACuC is greater than the Zeeman energy by a factor of about 2 allowing nonsecular dipole-dipole contributions to M_2. In this case we would expect $\rho \sim 0$. Although $J_0 \sim g\mu_B H_0$ at K band, the data is not significantly different than at X band.

The computer program used to fit Eq. (5) to the linewidth data employed an algorithm[14] which allowed nonlinear least-squares fits to arbitrarily complex functions. The angular dependence of errors in the linewidth measurements was included to improve the least-squares fit. Inclusion of next-nearest neighbors in the five-parameter fit had little effect on the generated parameters. Only by including the $S \times S$ term and lowering the symmetry of the D_e^{mol} could a fit be obtained, and in all cases it was found that the best fit was made with $\rho=0$ and $\alpha=0$. A plot of the five-parameter fit is shown in Fig. 3 with the calculated value of $D_d=0.056$ K and the fitted values of $J_0=0.80$ K, $D_e=0.032$ K, $\Delta=8.1$, $d=0.043$ K, and $\theta_A=27°$.

IV. DISCUSSION

Stirrat *et al.* have quoted linewidths in TMACuC of 250 G,[3] which is at least twice as large as our greatest linewidth value. Although the reason for this discrepancy is unknown, we noted that two crystal flaws dramatically altered the resonance linewidths, namely twinning and decomposition. The latter was studied through thermogravimetric analysis where we discovered that TMACuC dehydrates slowly at room temperature. This dehydration was accelerated by both temperature and direct, intense light. Crystals kept more than a year at room temperature exhibited significant decomposition. Therefore, we obtained all EPR data from newly grown crystals. To eliminate twinned or occluded crystals we chose samples which showed good extinction under polarized light. With good samples the angle dependence of the linewidths is reproducible to ±4 G. A similar angle dependence is observed in several other low-dimensional magnetic systems but probably the closest similarity is seen in copper benzoate trihydrate $[Cu(benz)_2 \cdot 3H_2O]$ as studied by Date *et al.*[15] and analyzed by McGregor and Soos.[4]

The magnetic system of TMACuC is more complicated than copper benzoate and other previously studied systems for several reasons. First, since J_0 is the order of $g\mu_B H_0$, the field dependence of the linewidths[16,17] may have an effect unaccounted for in this analysis: However, the present fit is qualitatively good and at least as good for either X-band or K-band data. Second, since no temperature region was found where the linewidths were temperature independent, it was necessary to allow J_0 to serve as one of the parameters in the least-squares fit. Finally, since the symmetry of the copper sites allows the $S \times S$ interaction, it should be included in the spin Hamiltonian. Only upon the inclusion of the latter interaction and a lowering of symmetry to orthorhombic did the fit qualitatively reproduce the linewidth data. The parameters obtained from the least-squares fit indicate that the relative magnitudes of the isotropic exchange, dipole-dipole, symmetric anisotropic, and $S \times S$ interactions are $J_0{:}D_d{:}|D_e|{:}|d|=1.0{:}0.07{:}0.04{:}0.05$. The interchain exchange in the hydrogen-bonding direction, according to Algra *et al.*, is a factor of 20 smaller than the intrachain exchange. However, because the chains so linked all have the same magnetic orientation, this exchange is lost in the larger intrachain exchange narrowing. The interlayer coupling was estimated by Algra to be almost a factor of 100 smaller than the intrachain coupling. As shown by Pople[17] this is far too small to cause any significant interactions, and the lines remain distinct. Because of the different orientations of the chains, the line position and widths as a function of angle gave no interpretable data, so no linewidth fit about the a and c axes was attempted.

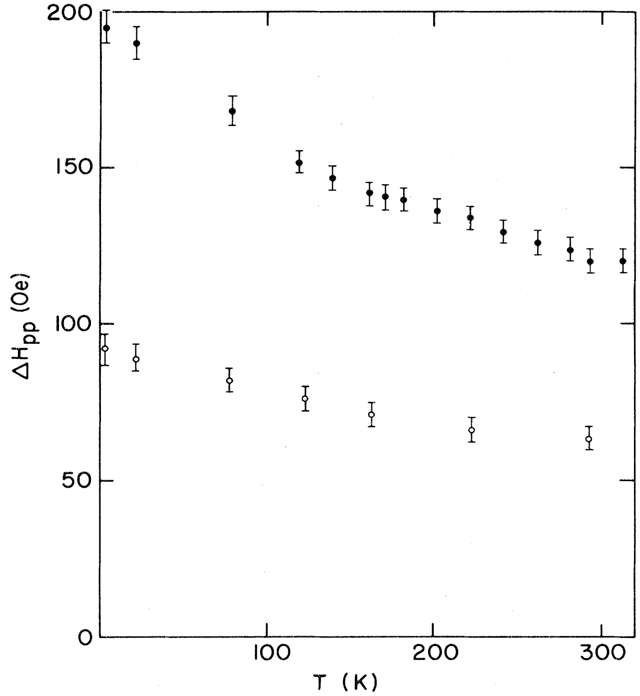

FIG. 5. Temperature dependence of $\Delta H_{pp}(\theta)$. Open circles are for $\theta=112°$ and the closed circles are data at $\theta=62°$.

It is instructive to compare the value of J_x determined by Algra *et al.* to our corresponding value of J_0 found from the linewidths calculations, as well as to compare the ratios of the isotropic to the anisotropic exchange determined by the two different methods. The value we obtained for J_0, 0.80 K, is about equal to the value they quote. Our value, however, was derived from a best fit using room-temperature data. This is important as the data show a strong (anomalous) temperature dependence of the linewidth, shown in Fig. 5: There is significant increase in linewidth as the temperature is lowered to 4 K. Part of this increase may lie in the temperature dependence of M_2 itself, owing to the lattice contraction and the resulting increased dipolar interaction. This would only account for about a 15% change in ΔH. On the other hand, assuming the simple $\Delta H_{pp} \propto M_2/J_0$ of Anderson, and assuming the temperature dependence is entirely in the isotropic exchange itself, the broadening can be explained by a J_0 that reduces by about 40%, or $J_0(4\ \mathrm{K}) \cong 0.5$ K. Since Algra *et al.*, derived their number from low-temperature data, our value does not compare so well. However, to check our assumption of temperature dependence, we used the low-temperature value of J_0 and held all other interactions constant with the result that the curve of ΔH vs θ

matched our low-temperature data very well. A rise in linewidth could be expected for a 1D ferromagnetic according to Richards[18] if a diffusive model were operative; however, even then most of the increase would occur within a few factors of T_c, or in the case of TMACuC, only below 10 K or so. A more likely explanation is seen in Table II which shows a distinct temperature dependence of the orientation of the g tensor undoubtedly owing to structural changes with temperature. This implies a possible change with temperature in the Cu—Cl—Cu bond angle which, according to Jansen and Block,[19] can have a profound influence on the magnitude and the character of the symmetric exchange. Table II also shows a measurable change in the values of the g tensor with temperature which implies a temperature dependent Jahn-Teller distortion. Khomskii and Kugel[20] have recently shown that a phonon modulation of the Jahn-Teller distortion could give rise to a temperature-dependent isotropic exchange. Although it is possible that a structural reorientation would effect both the anisotropic and the antisymmetric contributions to M_2, it does not seem likely in this case since the angle dependence at low temperature remains almost exactly the same as at room temperature.

Because of the large value of Δ, the matrix D_e^{mol} gives an unexpected result. Instead of displaying anisotropy, which favors the Z direction as might be expected from the g-value anisotropy, the values of p and q are large, which implies a significant XY-like character to the exchange insofar as the orientation of D_e^{mol} allows such an interpretation. This also seems to be not inconsistent with the results of Algra *et al.*, who required a 10% reduction of the magnetic susceptibility along the chain, claiming that a small Ising-type contribution was necessary to fit their data. Our data can be interpreted as allowing about 12% XY character to the exchange. Finally the difference between p and q gives the departure from axial symmetry, which is of the order of D_e.

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