PHYSICAL REVIEW B VOLUME 35, NUMBER 1 1 JANUARY 1987

Paramagnetic susceptibilities of the antiferromagnetic quantum chain copper chloride bis—dimethyl sulfoxide: Theory and experiment

C. P. Landee, A. C. Lamas, and R. E. Greeney
Department of Physics, Clark University, Worcester, Massachusetts 01610

K. G. Bücher*
Fakultät für Physik der Universität Freiburg, Hermann-Herder Strasse 3, D-7800 Freiburg im Breisgan, West Germany

(Received 7 July 1986)

Copper chloride bis(DMSO) (DMSO is dimethyl sulfoxide) consists of linear chains of antiferromagnetically coupled $S=\frac{1}{2}$ ions. The single-crystal dc magnetic susceptibilities of both protonated and deuterated samples of this compound have been measured between 1.8 and 45 K; the susceptibilities of the two versions were identical. Evidence for a small amount of Ising-like anisotropy was seen in the temperature-dependent susceptibilities. The data were compared to the predictions of Bücher and Honerkamp for the behavior of single-crystal susceptibilities of *XXZ* linear chains. Good agreement was found for an exchange strength of $J/k_B=-8.25$ K and an anisotropy parameter $\Delta=1.1$, slightly Ising-like. The *b* axis is the easy axis. The results of further theoretical studies on the effect of *XXZ* anisotropy upon powder susceptibilities of linear chains are presented. A procedure is described for determining both J and Δ for *XXZ* antiferromagnetic chains from powder data.

I. INTRODUCTION

Quantum magnetic linear chains continue to be of interest to both theorists and experimentalists. These chains are defined by the *XXZ* Hamiltonian which describes anisotropic interactions between nearest-neighbor quantum ($S=\frac{1}{2}$) spins:

$$\mathscr{H}=-2J\sum_{i=1}^{N}(S_i^xS_{i+1}^x+S_i^yS_{i+1}^y+\Delta S_i^zS_{i+1}^z)\ . \qquad (1)$$

$\Delta=0$ corresponds to the planar (XY) limit, while $\Delta=1$ and $\Delta=\infty$ correspond to the isotropic (Heisenberg) and the axial (Ising) limits, respectively. While the static properties of the *XY* and Ising linear chains can be solved exactly,[1] the analysis of the Heisenberg antiferromagnet (HB AF) has remained a challenge. No analytical expression has been found for any of the static or dynamic properties. The first calculations of the susceptibility and specific heat were reported in a now celebrated 1964 paper by Bonner and Fisher[2] who used extrapolated results based on machine calculations for finite chains.

Experimental realizations of magnetic linear chains are never found to be either perfectly isotropic or anisotropic. Knowledge of the influence of exchange anisotropy upon the thermodynamic functions for arbitrary values of Δ is therefore important for the analysis of experimental data. The Bonner-Fisher techniques have been employed independently by Blöte[3] and de Neef[4] to study the influence of anisotropy upon the magnetic specific heat. The dependence of the single-crystal susceptibilities upon Δ have recently been calculated by Bücher and Honerkamp[5] (BH) using similar techniques. The excitation spectrum as a function of Δ has been determined by Schneider *et al.*[6] who used the results to study the spin-correlation functions.

A new approach for studying the low-temperature properties of quantum spin chains has recently been developed by Müller and coworkers.[7,8] For the isotropic case, the existence of strong quantum fluctuations leads to a spin-wave double continuum of excited states, which dominates the dynamical correlation functions. The application of a magnetic field leads to further novel features, such as the existence of a soft mode which moves across the Brillouin zone as the field is increased. These features are solely due to the presence of the quantum fluctuations and invalidate the classical spin-wave theory description of the dynamical behavior.[8,9]

These significant predictions have yet to be confirmed by experimental study. Such confirmation through neutron scattering requires a model system consisting of well-isolated linear chains of spin-$\frac{1}{2}$ ions, coupled by antiferromagnetic exchange and without significant anisotropy. In the first neutron scattering experiments on a spin-$\frac{1}{2}$ HB AF, a sample of copper chloride bispyridine (CPC) was studied both in zero[10] and applied magnetic field.[11] Asymmetric line shapes were observed, in accordance with the theoretical predictions,[8] but the unavailability of sufficiently large single crystals and the large value of the exchange constant ($J/k_B=-13.2$ K) for CPC ruled it out as a suitable system for more detailed studies. A more promising candidate is copper chloride bis(DMSO), $CuCl_2\cdot 2DMSO$ (CDC) [DMSO is dimethyl sulfoxide, $(CH_3)_2SO$], which is readily available as large single crystals. Results of a preliminary neutron scattering study on CDC have recently been reported.[12]

The structure of CDC (orthorhombic, space group *Pnma*, $a=8.054$ Å, $b=11.546$ Å, and $c=11.367$ Å, respectively) was shown[13] to consist of $CuCl_2(DMSO)_2$ molecules tied together into chains along the *a* axis by a long Cu—Cl bond (Fig. 1). The *a* axis is thus the path-

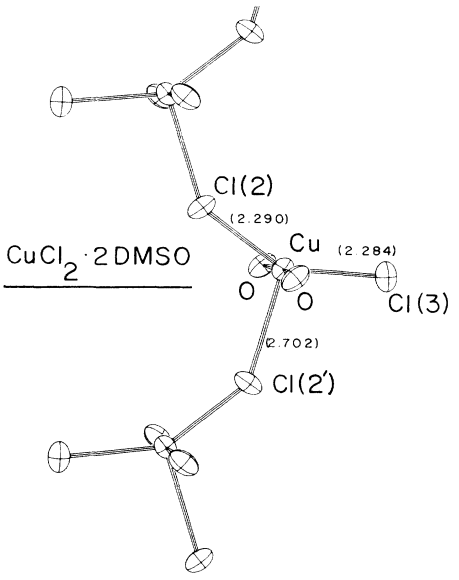

FIG. 1. The structure of the chloride-bridged chain in CDC is shown. The *a* axis is vertical. The chain has been rotated by 8° about the *a* axis to allow the copper and oxygen sites to be seen clearly. Prior to the rotation the *c* axis was horizontal and the *b* axis was normal to the page. The copper atoms are bonded to the two oxygens of the DMSO groups, the terminal chloride, Cl(3) and the bridging chloride, Cl(2). In addition, the axial site of the copper ion is occupied by the bridging chloride of the adjacent copper. All distances are given in angstroms.

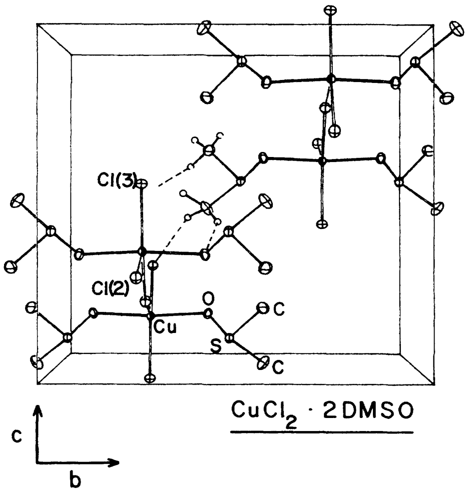

FIG. 2. The unit cell of CDC is shown, viewed down the chain *a* axis. The *b* axis is horizontal and the *c* axis is vertical. The copper and chloride sites are located on mirror planes at $\frac{1}{4}b$ and $\frac{3}{4}b$. Only some of the hydrogen positions are shown for purposes of clarity. The packing of the DMSO groups between the chains allows contacts between hydrogen sites of one chain and ions of another. Contacts of less than 3.0 Å are indicated by dashed lines.

way for the dominant intrachain superexchange interaction. A second, symmetry-related chain is located in the bottom half of the unit cell. The chains are separated by the bulk of the DMSO groups. Hydrogen bonding occurs between the methyl group hydrogen atoms and both the chloride and oxygen atoms of neighboring chains, providing a pathway for interchain magnetic interactions (Fig. 2). The ultimate transition to long-range magnetic order is induced by these interactions. The axes of the resulting quasiplanar $CuCl_2O_2$ groups point alternately 22° on either side of the *a* axis due to a 2_1 screw axis parallel to the *a* axis. The *g* factors have been found to be 2.31, 2.02, and 2.14 along the *a*, *b*, and *c* axes, respectively.[14]

The magnetic susceptibility of CDC was first measured for powdered samples.[15] The data agreed with the predictions of a pure spin-$\frac{1}{2}$ HB AF model with an exchange constant $J/k_B = -8.8$ K. No indication of ordering was seen in the dc measurements down to 2 K. Later single-crystal measurements,[16] done on protonated samples, showed the presence of slight anisotropy, with the *b* axis preferred. The data were interpreted in terms of the new results of Bücher and Honerkamp,[5] which showed there to be approximately 10% Ising-like anisotropy. No quantitative fits were made to that data in terms of the BH predictions. The single-crystal measurements, likewise performed in static fields, showed no anomalies down to 1.8 K.

The ordering temperatures of CDC have recently been determined and have been found to contain a strong isotope dependence. The neutron experiments[12] on a deuterated sample of CDC have found $T_N = 0.93$ K, while ac susceptibility measurements[17] on a protonated sample show $T_N = 2.7K$. The presence of spin canting is indicated by both sets of experiments. The origin of this large isotope dependence of the ordering temperature is currently under investigation and results will be presented elsewhere. The large difference in ordering temperatures suggested the possibility of further differences in the magnetic behavior of the two versions of CDC. In the present paper we report on new studies of the paramagnetic single-crystal dc susceptibilities of deuterated CDC, CDC(d) and compare them to those of the protonated version, CDC(p). The data are quantitatively compared to the predictions of Bücher and Honerkamp as a way of determining both the exchange parameter and the extent of exchange anisotropy. We also report on an extension of the original BH paper to include the effect of anisotropy upon powder susceptibilities.

II. EXPERIMENTAL

A. Sample information

Single crystals of both protonated and deuterated versions of CDC have been obtained through slow evaporation of methanol solutions of anhydrous copper chloride and the appropriate DMSO in a 1:2 molar ratio.[13] The deuterated DMSO (Ref. 18) was 99.8% isotropically pure. Crystals several cubic centimeters in volume can be obtained with care. The crystals grow as green rectangular plates with well-developed (001) faces and extended along the a axis. Neutron scattering experiments[12] on powdered samples and single crystals have shown the symmetry of the unit cell to be unchanged upon deuteration. A full crystal structure determination of both versions at low temperature is in progress.

Examination under polarized light show the crystals to be pleochroic. When polarized light is transmitted parallel to the c axis (i.e., through the plates) with the electric field vector parallel to the chain axis **a**, the transmitted light is emerald green. Rotating the crystal by 90° about **c**, thereby bringing the polarization axis parallel to **b**, changes the color of the transmitted light to a more yellow hue.

B. Magnetic measurements

The single-crystal dc susceptibilities of both deuterated and protonated versions of CDC have been measured between 1.8 and 45 K using a PAR model 155 vibrating-sample magnetometer. Sample temperatures were measured with a calibrated carbon-glass resistance thermometer while magnetic field strengths were determined with a commercial Hall-probe gaussmeter.[19]

The magnetizations along all axes of the two versions of CDC were found to be linear with field up to the maximum field of 10 kOe. The crystal axes were identified with polarized light before mounting on the sample rod. The alignment of the axis with the applied field was verified by rotating the samples and determining the angular dependence of the magnetization. The extrema found corresponded to the initial alignment within 10°. The dc susceptibilities were computed as the ratio of M/H. Corrections have been made for diamagnetism and the temperature-independent paramagnetic of the copper ion. The data have also been corrected for the angular-dependent background signal, measured independently. Uncertainty in this correction leads to an uncertainty of several percent in the absolute magnitudes of the reported results.

III. RESULTS AND DISCUSSION

In this section the experimental results for the paramagnetic susceptibilities are reported and interpreted. The experimental results are discussed in Sec. III A while the theoretical analysis of the influence of anisotropy is discussed in Sec. III B; single-crystal susceptibilities are the subject of Sec. III B 1, while new results are reported for powder susceptibilities in Sec. III B 2. The procedure for extracting a set of parameters $\{\Delta, J, g\}$ from either single-crystal or powder susceptibilities is the subject of Sec. III B 3. The experimental data are then compared to the theoretical predictions in Sec. III C. The paper concludes with a comparison of CDC to other examples of the Heisenberg linear-chain antiferromagnet.

A. Experimental magnetic susceptibilities

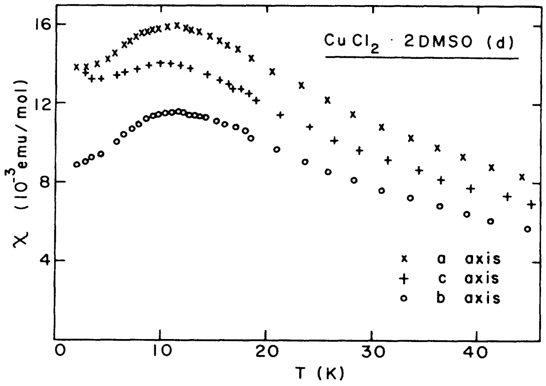

FIG. 3. The single-crystal dc susceptibilities of deuterated CDC are shown as a function of temperature. These are identical to the susceptibilities of the protonated samples studied previously.

The principal susceptibilities of deuterated $CuCl_2 \cdot 2DMSO$ are plotted versus temperature T in Fig. 3. Within experimental limits, these molar susceptibilities are identical to those of the protonated version of CDC reported previously.[16] The three susceptibilities display broad maxima at 11.1(2), 11.4(2), and 10.6(4) K along the a, b, and c axes, respectively. The magnitudes of the susceptibilities are in accordance with the reported g factors; $\chi_a > \chi_c > \chi_b$. The ratio of the susceptibilities is not, however, in the ratio of the squares of the g factors, as would be expected for a purely Heisenberg system. Below 10 K, χ_b decreases at the greatest rate but has only decreased 24% from its maximum value by 1.8 K. The chain-axis susceptibility χ_a is constant below 4 K while χ_c reaches a minimum at 4 K and increases to a value of 0.0138 emu/mol at 1.8 K, where it equals χ_a.

Since the ordering temperature of CDC(p) has been reported[17] to be 2.7 K, the dc susceptibilities of that version were carefully restudied in the helium region. No anomalies or changes of slope were seen in the data along any of the axes. The dc susceptibilities of the protonated version (for which ordering does occur above 1.8 K) and the deuterated version (with no such ordering) were identical.

B. Theory of susceptibilities of anisotropic quantum chains

Starting from the Hamiltonian (1) the susceptibilities parallel or perpendicular to the easy axis are readily derived by exact sum rules or perturbation calculations to be

$$\chi_{\parallel}(T) = N\frac{(g_{\parallel}\mu_B)^2}{k_B T}\int d\omega\, S_{\parallel}(0,\omega,T) \equiv \frac{N g_{\parallel}^2 \mu_B^2}{J}\chi_{\parallel}^r , \tag{2}$$

$$\chi_{\perp}(T) = N(g_{\perp}\mu_B)^2 \frac{2}{J}\int \frac{d\omega}{\omega} S_{\perp}(0,\omega T) \equiv \frac{N g_{\perp}^2 \mu_B^2}{J}\chi_{\perp}^r . \tag{3}$$

The perpendicular susceptibilities can be split into $\chi_{\perp,1}\chi_{\perp,2}$ by anisotropic g factors.

The structure functions $S(q,\omega,T)$ are determined by direct diagonalization of (1) for short chain lengths to be

$$S_\nu(q,\omega,T)=\frac{1}{Z}\sum_{\lambda,\lambda'} e^{-E_\lambda/k_BT}\delta(\omega-(E_{\lambda'}-E_\lambda))\,|\langle\lambda|S_\nu(q)|\lambda'\rangle|^2,\ \text{where } \nu=||\text{ or }\perp\ . \tag{4}$$

Good accuracy is expected for the prediction of static properties, such as the susceptibilities, even for relatively short chain lengths. Comparison to the available exact results and previous work on finite chains indicates the lack of significant error in the predicted susceptibilities for relative temperatures $T^r\equiv kT/|J|$ greater than 0.5. For a detailed discussion of the numerical methods applied and the accuracies obtained, see Ref. 5.

1. Single-axis susceptibilities

The results from Ref. 5 for the effect of anisotropy upon the single-crystal susceptibilities are summarized in Fig. 4. Since the Hamiltonian used has *XXZ* symmetry, the following results always predict identical behavior for one pair of axes. Orthorhombic symmetry, with different temperature dependence along all three axes, cannot be explained by this model. Depending on the anisotropy (Ising, Heisenberg, planar) the single axis susceptibilities show maxima along one or more directions. For antiferromagnets, the maxima appear along all three directions. The anisotropy causes the susceptibility maxima along the easy and hard directions to appear at different temperatures. For the planarlike case, the maximum in $\chi_{||}$ appears a lower temperature than the two perpendicular susceptibilities [Fig. (4a)]. For axial anisotropies, the reverse is true [Fig. 4(b)]. In the case of ferromagnetic exchange, the differences are more striking. Planarlike (Ising) behavior manifests itself as a divergence in the easy-plane (easy-axis) susceptibility and a maximum (maxima) in the one (two) perpendicular components [Figs. 4(c) and 4(d)]. For the isotropic Heisenberg case, the temperature dependence of the susceptibilities along all three axes is the same, marked only by possible difference of magnitude due to g-factor anisotropy. In all cases, there are marked differences between these results and those of the classical $S=\infty$ model.

2. Powder susceptibilities

Powder susceptibilities have been calculated as

$$\begin{aligned}\chi_p(t)&=\tfrac{1}{3}\chi_{||}(T)+\tfrac{1}{3}\chi_{\perp,1}(T)+\tfrac{1}{3}\chi_{\perp,2}(T)\\&=\frac{N\mu_B^2}{3J}g_{||}^2[\chi_{||}^r(T)+g_s^2\chi_\perp^r(T)]\ ,\end{aligned}\tag{5}$$

where

$$g_s^2=(g_{\perp,1}^2+g_{\perp,2}^2)/2g_{||}^2\equiv g_\perp^2/g_{||}^2\ . \tag{6}$$

In Fig. 5 the reduced powder susceptibilities

$$\chi_p^r\equiv\frac{\chi_p(T)3J}{Ng_{||}^2\mu_B^2}\frac{1}{(g_{||}^2+g_{\perp,1}^2+g_{\perp,2}^2)} \tag{7}$$

are plotted against the relative temperature T^r for selected values of the anisotropy parameter. For small values of Δ the curves show pronounced maxima similar to that seen for the HB AF isotropic case, $\Delta=1$. The maxima appear at smaller relative temperatures as Δ is reduced (corresponding to more planarlike). As the system becomes more axial, the reduced powder susceptibility becomes only weakly dependent upon temperature, reflecting the behavior of the perpendicular susceptibilities of an axial magnet.

During the calculations, the squared ratio of the perpendicular to the parallel g factors given as g_s^2 in Eq. (6) has been restricted to the range $0.8<g_s^2<1.2$ to correspond to the range of g_s found for most $S=\frac{1}{2}$ linear-chain compounds. It has been found that, for a fixed Δ, varying g_s^2 by as much as 30% leads to only minor changes for the shape of the curves or the position of the maximum in Fig. 5. Therefore, only curves for $g_s^2=1$, corresponding to isotropic g factors, are given in Fig. 5.

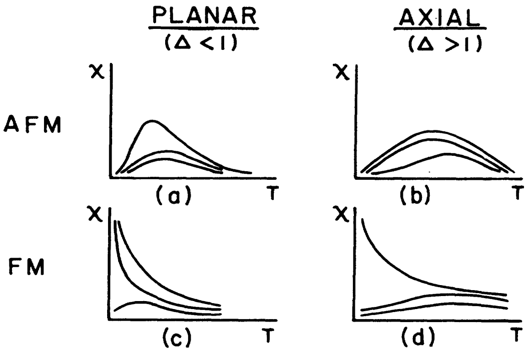

FIG. 4. The effect of anisotropy upon the principal susceptibilities is shown for the limiting cases of planar and axial symmetry for both the antiferromagnetic (AFM) and ferromagnetic (FM) cases.

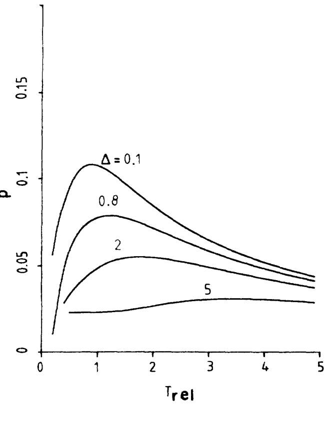

FIG. 5. The reduced powder susceptibilities of antiferromagnetic linear chains is shown as a function of the relative temperature $T^r=k_BT/|J|$ for several values of the anisotropy parameter. Values of Δ less than 1 correspond to the planar case.

3. *Extraction of model parameters for experiments*

Single-crystal susceptibility data can be analyzed according to the results of BH (Ref. 5) to arrive at an unambiguous assignment of Δ, J, and g. When only powder data are available, information is inevitably lost. Nevertheless, it is still possible to assign a unique set of values for at least certain ranges of the anisotropy parameter.

When single-crystal measurements of $\chi_{\parallel}$ and $\chi_{\perp}$ are available, Fig. 4 gives a first indication of the type of model appropriate for the compound: ferromagnetic or antiferromagnetic, planar or Ising-like. For antiferromagnets, the anisotropy parameter can be determined by the relative position of the maxima of the susceptibilities. Knowing the ratio of $T^{\parallel}_{\max}/T^{\perp}_{\max}$, the value of Δ can be obtained from Figs. 3(a)–3(c) in BH, Ref. 5. Given Δ, $|J|$ is found from the expression $|J|=k_B T^{\parallel}_{\max}/T^{r}_{\max}(\Delta)$, where curves for $T^{r}_{\max}(\Delta)$ are given in Figs. 3(d)–3(g) of the same reference. Finally, knowing both Δ and J, the g factors can be obtained from the curves for $\chi^{r}_{\max}T^{r}_{\max}$ in BH, Figs. 4 and 5.

This procedure yields a precise and unambiguous set of parameters. While both $\chi^{r}_{\max}$ and $T^{r}_{\max}$ are strongly dependent upon J as well as Δ, their product is a function of Δ alone, when evaluated at the maximum. This fact follows since

$$\chi(T)=\frac{\chi^{r}(\Delta)Ng^{2}\mu_B^{2}}{J}=\left[\frac{\chi^{r}(\Delta)T^{r}(\Delta)}{k_B T}\right]Ng^{2}\mu_B^{2}\ . \tag{8}$$

Thus at the point of the maximum

$$\frac{(\chi_{\max}T_{\max})_{\text{expt}}}{Ng^{2}\mu_B^{2}}=\chi^{r}_{\max}(\Delta)T^{r}_{\max}(\Delta)\equiv G(\Delta)\ \text{for}\ \chi_{\parallel},\chi_{\perp},\chi_{p}\ . \tag{9}$$

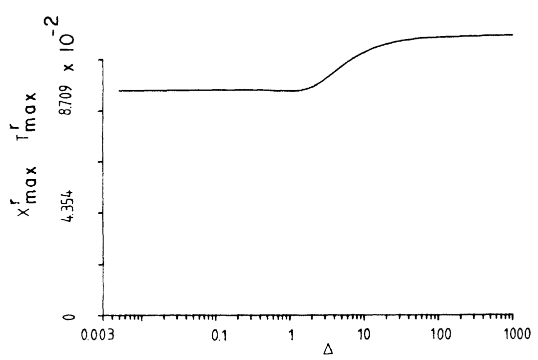

FIG. 6. The product of reduced powder susceptibility and reduced temperature evaluated at the maximum of susceptibility is plotted against the anisotropy parameter Δ. This product [defined as $G(\Delta)$ in the text] is insensitive to the value of Δ in the planar regime ($\Delta<1$), making an assessment of Δ impossible in this range. A reasonable dependence of the product is found in the Ising regime, allowing a determination of the anisotropy parameter from experimental data.

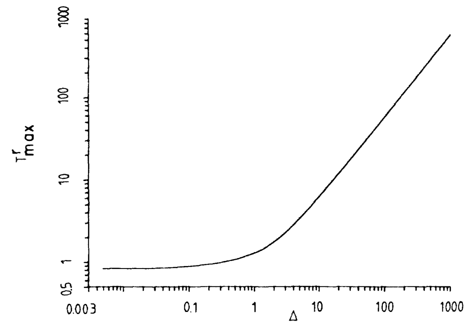

FIG. 7. The anisotropy dependence of the relative temperature at the maximum susceptibility, $T^{r}_{\max}$ is shown. $T^{r}_{\max}$ is defined as $k_BT/|J|$ evaluated at the temperature of the maximum susceptibility. The sensitive dependence of $T^{r}_{\max}$ upon Δ in the Ising regime is clear.

As shown in BH, $|G(\Delta)|$ is a uniquely determined function of the anisotropy parameter.

When considering powder susceptibilities, information is lost. Figures 6 and 7 show $|G(\Delta)|$ and $T^{r}_{\max}$ versus Δ, respectively, for the powder susceptibilities. As discussed above for the single axes susceptibilities, $|G(\Delta)|$ changes little with Δ, only about 25% over the entire parameter range of Δ and not at all for variation of Δ in the planar case ($\Delta<1$). Consequently, a unique set of parameters $\{\Delta, |J|\}$ is not possible for systems with planar anisotropy. When Ising-like anisotropy is present, the unique parameter set can be obtained by the following procedure, which is similar to that used for single crystals.

Knowledge of experimental value of $\chi_{\max}T_{\max}$ determines $G(\Delta)$ from Eq. (9), provided an average g factor is known (as from a EPR measurement). The unique value of Δ corresponding to $G(\Delta)$ can be determined from Fig. 6. Once Δ is known, the precise value of $T^{r}_{\max}$ is obtained from Fig. 7. $|J|$ is then equal to the ratio $k_B T^{\text{expt}}_{\max}/T^{r}_{\max}(\Delta)$.

It is noted that the sensitivity of the functions plotted for the powder case in Figs. 6 and 7 is low, which means precise values of J and Δ can never be well determined for systems which have only been studied as powders. Only in the case of Ising-like anisotropy is it possible to make even an imprecise assignment; it is not at all possible for the planar case. This assignment procedure is built upon the properties of $G(\Delta)$, which is a function of Δ alone. The dependence is unfortunately weak, which makes simultaneous assignment of Δ and J imprecise, although possible. Should an independent value exist for either Δ or J, however, the other parameter can be determined with good precision, since the powder susceptibility is strongly dependent on both Δ and J, as shown in Figs. 5 and 7.

C. Analysis of susceptibilities of $CuCl_2\cdot 2DMSO$(*d* or *p*)

The single axis susceptibilities of CDC have been analyzed according to the procedure described in Sec. III B 3 above. Since the protonated and deuterated versions have the same dc susceptibilities, the following analysis applies to both equally, even though the data sets under analysis in this article correspond to CDC(d). The easy axis corresponds to b since the susceptibility reaches its peak along **b** at a higher temperature than along **a** or **c**. In addition, χ_b continues to drop with decreasing temperature while the susceptibilities along **a** and **c** level off below 4 K. We note the data reflect the orthorhombic character of CDC in that the two $T_{\max}^{\perp}$'s corresponding to **a** and **c** are not equal (being 11.1 and 10.6 K). The difference between them is as large as the difference between the larger of them and $T_{\max}^{\parallel}$ along **b**, 11.4 K. From the ratios $T_{\max}^{\parallel}/T_{\max}^{\perp}$ and the information contained in Fig. 3(b) of BH, values of Δ of either 1.04 or 1.13 are indicated, depending on the choice of $\chi_{\perp}$. The lower anisotropy leads to a value of $|J/k_B| = 8.6(1)$ K while the upper value indicates 8.2(15) K.

A satisfactory fit to the data along all three axes may be made using an anisotropy value of $\Delta = 1.1$, $J/k_B = -8.25$ K and g factors equal to 2.28, 1.97, and 2.12 respectively, for a, b, and c axes. These g factors are in good agreement with the experimental EPR values[14] of 2.30, 2.02, and 2.10, respectively. The theoretical fits are shown in Fig. 8. It is seen that the model prediction fits the data well at the high-temperature end and over the hump. Below 8 K the predicted curves fall systematically below the data. The predicted curves are only continued down to 4 K since that temperature corresponds to the lowest value of the reduced temperature $k_B T/J$ for which the machine calculations are reliable.

We attribute the discrepancies between the model and data at lower temperatures to the existence of spin canting within CDC and not to the onset of long-range order. Both the neutron scattering data[12] and the ac susceptibility data[17] show that the spins maintain components along all three axes in the ordered state. Such canting is allowed by the presence of the 2_1 axis along the chains. The canting thus leads to the existence of components along all three axes and explains why the experimental susceptibilities in all cases lie above the predicted values. Thus the b axis is the preferred axis in the bulk material but not necessarily the local axis at the metal site. Such behavior is commonly seen in canted magnets.[20]

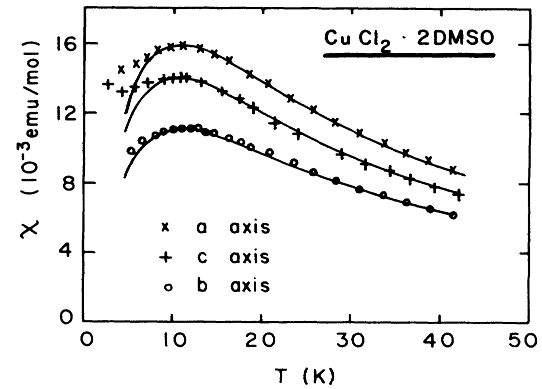

FIG. 8. The experimental single-crystal susceptibilities for the deuterated version of CDC are compared to the theoretical predictions with parameters $J/k = -8.25$ K and anisotropy parameter $\Delta = 1.1$. The theoretical g factors used were 2.30, 2.12, and 1.97 for the a, c, and b axes, respectively. Only half of the experimental data points are plotted in this figure.

The discrepancy between data and model cannot be due to the influence of exchange between the chains since the dc susceptibilities of the deuterated and protonated versions of CDC are identical even though the transition temperatures differ by a factor of three. Should this discrepancy be due to interchain coupling, it would be expected that the susceptibilities of the protonated version, ordering at 2.7 K, would have deviated for the model predictions at higher temperatures than the deuterated version, ordering at 0.9 K. Since this is not the case, we attribute the deviations observed to the existence of the canting.

We conclude that CDC can be described as an antiferromagnetic chain with $J/k_B = -8.25$ and a slight amount of Ising-like anisotropy, $\Delta = 1.1$. A small and unknown amount of hidden spin canting is also present.

D. Comparison to other Heisenberg antiferromagnetic chains

The applicability of a compound as a model system to test predictions for the HB AF model depends on a number of factors which include the degree of one-dimensional isolation, the amount of deviation from pure isotropic exchange, and the availability of suitable single crystals.

A purely one-dimensional magnetic system will not undergo a transition to long-range order at any finite temperature. However, in all physical realizations, a certain amount of three-dimensional interaction is inevitable. This interaction, characterized by the parameter J', may at the very least have its origin in dipolar fields and will induce a state of long-range order with the critical temperature T_c related to the ratio $R = J'/J$. The ordering temperature can be estimated as the temperature at which the available thermal energy equals the exchange energy between correlated segments on adjacent chains.[21,22]

$$k_B T_c / |J| = \xi(T_c) R S(S+1) \ . \qquad (10)$$

$\xi(T)$ is the correlation length within the chain which, for the Heisenberg chain equals $2|J|S(S+1)/k_B T$. It follows that

$$k_B T_c / |J| \approx \sqrt{R} \ . \qquad (11)$$

The presence of any exchange anisotropy increases the correlation length of a chain for a given T'; consequently, for a given $|J|$ and T_c, the above relation provides an upper bound for R. A rule of thumb is that adequate one-dimensional isolation is often found in systems with $R < 10^{-2}$.

In Table I, the available experimental information on a number of $S = \frac{1}{2}$, antiferromagnetic, quasi-Heisenberg linear chain compounds is tabulated, along with the ratio $k_B T_c / |J|$ and the value of R obtained from relation (11). The recently studied copper pyrazine nitrate[23] is currently the most isolated example known of a one-dimensional magnetic chain but has not been prepared in

TABLE I. Quasi-Heisenberg antiferromagnetic $s=\frac{1}{2}$ linear chains. pyz is for pyrazine, py is for pyridine, and DMSO is dimethyl sulfoxide.

Compound	$-J/k_B$ (K)	T_c (K)	$k_BT_c/\vert J\vert$	$R\equiv\vert J'/J\vert$	Comments	Ref.
$Cu(pyz)(NO_3)_2$	5.20	<0.05	<0.01	$<10^{-4}$	Needle-like crystals	23
$Cu(py)_2Cl_2$ (CPC)	13.4	1.13	0.08	7×10^{-3}	Needle-like crystals	24
$CuSO_4\cdot5H_2O$	1.45	0.035	0.024	6×10^{-4}	Two inequivalent copper sites, strong field dependence of T_c	1, 25
$CuSeO_4\cdot5H_2O$	0.85	0.045	0.053	3×10^{-3}	Same as the sulfate above	1, 25
$Cu(NH_3)_4SO_4\cdot H_2O$ (CTS)	3.15	0.43	0.137	1.9×10^{-2}	Possibly 2d magnet	26, 27
$Cu(NH_3)_4(NO_3)$ (CTN)	3.9	0.15	0.038	1.4×10^{-3}	No anisotropy observed	28
$Cu(DMSO)_2Cl_2$ (CDC)	8.3	0.92(*d*) 2.7 (*p*)	0.11 0.32	1.2×10^{-2} 10×10^{-2}	somewhat Ising-like, 3d crystals	Present work 15

single crystals suitable for neutron scattering. Copper bis—pyridine dichloride[24] (CPC) is more poorly isolated ($R\approx0.007$), but no evidence of three-dimensional correlations were seen in the neutron scattering experiments provided the measurements were made at $T>1.5T_c$, (Refs. 10 and 11), CPC is likewise limited by an inability to be crystallized in suitable volume.

Compounds which are available as larger single crystals include copper sulfate pentahydrate,[25] copper selenate pentahydrate,[25] and copper tetrammine sulfate monohydrate.[26] The exchange within the pentahydrate salts is weak and renders experiments at low reduced temperature more difficult. The tetrammine[26] compound is frequently cited as an example of a one-dimensional HB AF but a number of papers have questioned whether it behaves more as a two-dimensional magnetic system.[27] The anhydrous copper tetrammine nitrate (CTN) consists of well-isolated chains, has been prepared as large single crystals and no anisotropy was observed in the single-crystal susceptibilities.[28] It would appear to be the ideal candidate for neutron scattering studies.

Copper chloride bis(DMSO) (CDC) is readily grown as large single crystals and, for the deuterated version, contains adequate isolation between the chains. A sensitive test for the presence of three-dimensional (3d) correlations is an examination of the neutron scattering cross section for momentum transfer perpendicular to the chain.[29] For a purely one-dimensional system the cross section is independent of these components, leading to planes of scattering. As three-dimensional correlations grow, the planes contract into Bragg points. For all temperatures greater than 1.2 K (i.e., for $T>1.3T_c$), planes of scattering were observed for CDC(*d*), indicating adequate one-dimensionality. Similar behavior was observed in the neutron scattering experiments[30] on copper chloride monoDMSO which is a ferromagnetic chain with an R of 3.4×10^{-2}. We can conclude that an exchange ratio R of several percent or less is capable of providing good one-dimensionality.

A surprising finding of this research has been the identical behavior of the dc paramagnetic susceptibilities of the protonated and deuterated versions of CDC. Evidently the presence of additional three-dimensional interactions in CDC(p) plays an insignificant role in the determination of the susceptibility of antiferromagnetic chains. Further experiments on the specific heat and linear magnetic birefringence on the two versions are in progress to test the influence of the J'/J ratio upon these features.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation, Grant No. DMR-8306432 and by the Research Corporation. The magnetometer was purchased with a grant from the NSF College Research Instrumentation Program. We thank Urs Geiser and Roger Willett for the preparation of the crystal structure drawings. We further thank Richard Carlin for permission to cite his unpublished results on the ordering temperature of CDC(p).

---

*Present address: Technische Universität Berlin, Institut für Werkstoffe der Elektrotechnik, Jebenstrasse 1, D-1000 Berlin 12, West Germany.

[1] L. J. de Jongh and A. R. Miedema, Adv. Phys. **23**, 1 (1974).
[2] J. C. Bonner and M. E. Fisher, Phys. Rev. **135A**, 640 (1964).
[3] H. W. J. Blöte, Physica **79B**, 427 (1975).
[4] T. de Neef, Phys. Rev. B **13**, 4141 (1976).
[5] K. Bücher and J. Honerkamp, Phys. Rev. B **28**, 373 (1983); K. G. Bücher, Ph.D. thesis, Universität Freiburg, 1984 (Internal Report, THEP 8214, available upon request).
[6] T. Schneider, E. Stoll, and U. Glaus, Phys. Rev. B **26**, 1321 (1982).
[7] G. Müller, H. Beck, and J. C. Bonner, J. Appl. Phys. **50**, 7404 (1979).
[8] G. Müller, H. Thomas, H. Beck, and J. C. Bonner, Phys. Rev. B **24**, 1429 (1981).
[9] J. H. Taylor and G. Müller, Phys. Rev. B **28**, 1529 (1983).
[10] Y. Endoh, G. Shirane, R. J. Birgeneau, P. M. Richards, and S.

L. Holt, Phys. Rev. Lett. **32**, 170 (1974).

[11] I. U. Heilmann, G. Shirane, Y. Endoh, R. J. Birgeneau, and S. L. Holt, Phys. Rev. B **18**, 3530 (1978).

[12] M. Roy, S. Satija, J. D. Axe, and C. P. Landee, Bull. Am. Phys. Soc. **30**, 573 (1985).

[13] R. D. Willett and K. Chang, Inorg. Chim. Acta **4**, 447 (1970).

[14] T. R. Reddy and R. Srinivsan, J. Chem. Phys. **45**, 2714 (1966). Note that the *b* and *c* axes in this paper are reversed compared to the convention of Ref. 12.

[15] W. E. Estes, W. E. Hatfield, J. A. C. van Ooijen, and J. Reedijk, J. Chem. Soc. (London), Dalton Trans. **1980**, 2121 (1980).

[16] C. P. Landee, A. C. Lamas, R. E. Greeney, and P. S. Gahlawat, J. Appl. Phys. **55**, 2473 (1984).

[17] R. L. Carlin (private communication).

[18] KOR Isotopes, Cambridge, Massachusetts.

[19] C. P. Landee, R. E.Greeney, and A. C. Lamas (unpublished).

[20] H. A. Groenendijk and A. J. van Duyneveldt, Physica **115B**, 41 (1982).

[21] J. Villain and J. M. Loveluck, J. Phys. Lett. **38**, 707 (1977).

[22] This discussion is based upon a similar analysis in Ref. 23.

[23] G. Mennenga, L. J. de Jongh, W. J. Huiskamp, and J. Reedijk, J. Magn. Magn. Mater. **44**, 89 (1984).

[24] W. Duffy, Jr., J. E. Venneman, D. L. Strandburg, and P. M. Richards, Phys. Rev. B **9**, 2220 (1974); R. C. Hughes, B. Morosin, R. M. Richards, and W. Duffy, Jr., *ibid.* **11**, 1795 (1975).

[25] L. S. J. M. Henkens, K. M. Diederix, T. O. Klaassen, and N. J. Poulis, Physica **83B**, 147 (1976), and references therein.

[26] T. Haseda and A. R. Miedema, Physica **27**, 1102 (1961); R. B. Griffiths, Phys. Rev. **135**, A659 (1964); S. Saito, J. Phys. Soc. Jpn. **26**, 1388 (1969).

[27] M. Date, M. Motokawa, H. Hori, S. Kuroda, and K. Matsui, J. Phys. Soc. Jpn. **39**, 257 (1975); W. Duffy, Jr., F. M. Weinhaus and D. L. Strandburg, Phys. Lett. **59A**, 491 (1977); see also Y. Ajiro, Y. Nakajima, Y. Furukawa, and H. Kiriyama, J. Phys. Soc. Jpn. **44**, (1978).

[28] S. N. Bhatia, C. J. O'Connor, R. L. Carlin, H. A. Algra, and L. J. de Jongh, Chem. Phys. Lett. **50**, 353 (1977).

[29] R. J. Birgeneau, R. Dingle, M. T. Hutchings, G. Shirane, and S. L. Holt, Phys. Rev. Lett. **26**, 718 (1971).

[30] S. K. Satija, J. D. Axe, R. Gaura, R. D. Willett, and C. P. Landee, Phys. Rev. B **25**, 6855 (1982).