PHYSICAL REVIEW B VOLUME 10, NUMBER 1 1 JULY 1974

Single-crystal magnetic-susceptibility measurements on the nearly two-dimensional Heisenberg system $[(NH_3CH_2CH_2)_2NH_2]$ $[CuCl_4]Cl$

D. Bruce Losee and William E. Hatfield
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514
(Received 9 November 1973)

The magnetic susceptibilities of both polycrystalline and single-crystal samples of the compound diethylenetriammonium chlorocuprate (II), $[(NH_3CH_2CH_2)_2NH_2]$ $[CuCl_4]Cl$, have been measured from 1.6 to 160 °K. The compound undergoes a phase transition to an antiferromagnetic state at 11.8 °K with the c crystallographic axis as the preferred axis. Above the transition, the magnetic properties of this material reflect its two-dimensional structural characteristics, with the predominate feature being a ferromagnetic alignment of spins within a network of isolated copper ions. The high-temperature polycrystalline data have been fitted to a variety of models for a quadratic lattice. When the data are fit to the two-dimensional Heisenberg model for the quadratic lattice, a value of $J/k = 18.7$ °K results. Although an excellent fit is achieved over a wide temperature range, the data are not able to discriminate between models in which there are variable degrees of anisotropy in the exchange. Finally, a comparison is made between $[(NH_3CH_2CH_2)_2NH_2]$ $[CuCl_4]Cl$ and the thoroughly studied $[C_2H_5NH_3]_2CuCl_4$.

INTRODUCTION

Renewed experimental interest in the magnetic properties of two-dimensional Heisenberg ferromagnets was initially stimulated by the theoretical findings of Stanley and Kaplan[1] and Mermin and Wagner.[2] From the high-temperature series-expansion results ($S \geq 1$) of Stanley and Kaplan, a new phase associated with the two-dimensional ferromagnet was proposed which is characterized by a divergence in the susceptibility at some transition temperature $T_c^{(2)}$. However, Mermin and Wagner rigorously proved that this isotropic two-dimensional Heisenberg system cannot possess spontaneous magnetization at a nonzero temperature and hence there can be no long-range order in the conventional sense. The question, then, remains whether or not it is possible to have a nonzero transition temperature $T_c^{(2)}$, characterized by a divergence in the susceptibility, yet below which no spontaneous magnetization exists. Of course, at some lower temperature, the system will experience the long-range-order effects from the ultimate three-dimensional realities of the crystal.

Since it has been known from Onsager's result[3] that the two-dimensional Ising model can support long-range order, it has been felt that the stabilization of the two-dimensional phase would depend, in some way, on the introduction of anisotropy into the lattice. Studies by Dalton and Wood[4] have explored a model which introduces anisotropic exchange into a Hamiltonian by an adjustable parameter and thereby has allowed a study of the approach to either the Heisenberg or Ising limiting cases. Their model predicts a finite transition temperature for the two-dimensional lattice with a finite amount of anisotropy, but the transition temperature tends toward zero logarithmically as the isotropic limit is approached.

The effects of anisotropic intralayer exchange have also been studied in the X-Y model. As its name implies, the direction of magnetization in this model is restricted to lie in the x-y plane. Theoretical results of Mermin and Wagner (as well as Oguchi[5]) for the two-dimensional lattice have shown that the pure X-Y model (isotropic exchange within the plane) cannot have a spontaneous magnetization above a nonzero temperature as was found for the analogous Heisenberg case. Furthermore, studies by Oguchi[5] and Ishikawa and Oguchi,[6] using an adjustable parameter in the exchange to explore the approach to either the Heisenberg, the Ising, or the X-Y limiting case, have postulated a divergent susceptibility at some transition temperature but no spontaneous magnetization for the pure X-Y case as observed for the pure Heisenberg case. From an examination of an exact high-temperature series expansion of the fluctuation in the long-range order, Betts *et al.*[7] have found that a transition temperature may exist for the X-Y model in two dimensions.

Recent theoretical work by Lines[8] utilizing wave-vector-dependent renormalization in a Green's-function formalism of the two-dimensional Heisenberg ferromagnet has shown that with the introduction of any finite amount of anisotropy, the model will support long-range order for any spin value and that $T_c \simeq T_c^{(2)}$ for small limiting values of the interlayer exchange and anisotropy within the layer. On the other hand, in the isotropic limit the result of Mermin and Wagner[2] is verified.

Quite recently, Kosterlitz and Thouless,[9] in proposing a new definition of order for two-dimensional systems called topological order, conjecture the existence of long-range order in the *X-Y* model but not in the Heisenberg model. Besides the introduction of some interlayer exchange interaction to stabilize these postulated "two-dimensional" phases, Fisher and Jasnow[10] have explored the stabilization effects of the finite sample size on this new phase as well as on the long-range order. A final note should be made of the recent theoretical work of Yamaji and Kondo,[11] who dispute the findings of Stanley and Kaplan and claim that the phase postulated by these authors is an artifact of the series truncation in the Heisenberg case for $S \geq \frac{1}{2}$.

The experimental problem, then, is one of exploring systems which nearly approximate a two-dimensional lattice and, within this framework, of exploring the effects of introducing small amounts of anisotropy in the intralayer exchange as well as the effects of varying the amount of interlayer exchange. In so doing, one can examine the theory as applied to the existence of this new phase, which has been characterized by a divergence in the susceptibility, as well as the possible coexistence of this new phase with the conventional long-range-ordered phase (spontaneously magnetized) and the paramagnetic phase.

The investigations[12-15] on the series of compounds $(C_nH_{2n+1}NH_3)_2CuCl_4$ ($n = 1, 2, 10$) at The University of Amsterdam have done much to clarify some of these predictions for the $S = \frac{1}{2}$ case. In this paper, the powder and single-crystal magnetic susceptibilities are reported for diethylenetriammonium chlorocuprate (II), $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$, a compound whose magnetic properties should reflect significant variations in interlayer coupling compared to the series previously reported.[12-15]

EXPERIMENTAL

Crystal characteristics

The compound diethylenetriammonium chlorocuprate, which was prepared by the published method,[16] crystallizes from an aqueous solution at room temperature in the orthorhombic space group *Pnma* with $a = 7.117$ Å, $b = 23.78$ Å, and $c = 7.342$ Å, and with four formula units per unit cell.[17] This material grows as rectangular rhombic prisms with faces (100), (010), (001) clearly revealed in this morphology. The b axis is perpendicular to the rectangular platelet, while the c axis is parallel to the shorter of the two sides that comprise this rectangular face. During the course of this investigation, the cadmium analog of this compound was prepared using a procedure similar to that used to prepare the copper salt. It was established by x-ray precession photographs that the cadmium compound is isomorphous to the copper compound with an identical morphology and the following cell constants: $a = 7.21$ Å, $b = 24.56$ Å, and $c = 7.26$ Å.

The structure of the copper compound has been shown[17] to consist of a two-dimensional network which is made up of square planar tetrachlorocuprate ions bridged by two additional chlorides from neighboring $[CuCl_4]^{2-}$ ions, thereby completing a distorted octahedron about each copper atom. The Cu–Cl atomic distances within the square planar unit are 2.276 and 2.272 Å, while the remaining Cu–Cl vector is 2.876 Å long and is nearly perpendicular to the square planar unit. These two-dimensional layers of copper atoms are separated one from another by more than 11.8 Å along the b axis by the protonated amine, the diethylenetriammonium ion, and the uncoordinated chloride ion. A nearly quadratic lattice ($c/a = 1.03$) of copper atoms is formed with the shortest copper–copper separation being 5.11 Å. An illustration of a portion of the unit cell is shown in Fig. 1, while a view of the two-dimensional network down the b axis is shown in Fig. 2.

Susceptibility measurements

Measurements of the magnetic susceptibility as a function of temperature were carried out in a

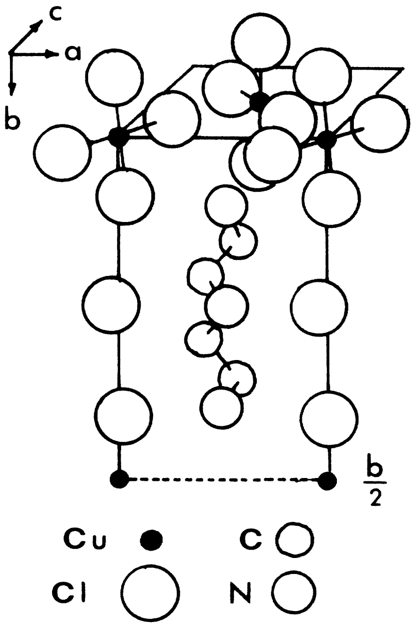

FIG. 1. View of the unit cell in $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$ which illustrates the two-dimensional character of the structure as well as the relative positions of the additional anionic chloride and protonated amine. For clarity only a portion of the unit cell is illustrated.

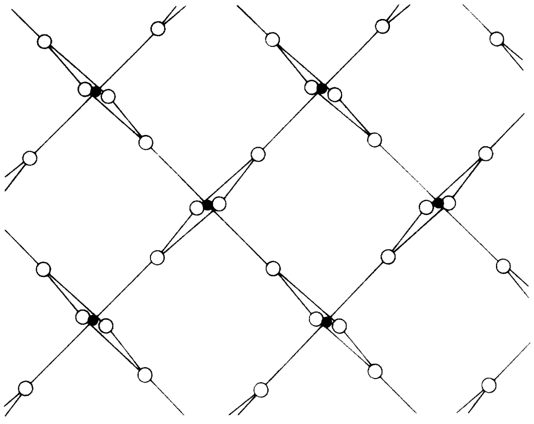

FIG. 2. View down the *b* axis (the *a* axis is vertical while the *c* axis is horizontal) with copper atoms represented as blackened circles and chlorine atoms as open circles. Only atoms constituting one layer of the two-dimensional network have been included.

stainless-steel variable-temperature Janis Dewar using a PAR vibrating sample magnetometer. The magnetometer was initially calibrated against $HgCo(NCS)_4$ using the recently reported[18] correction to the Weiss constant, and the calibration was later checked against a sample of $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$.[19] These two standards agreed to within 2%. It is felt that this represents the upper limit to the uncertainty in the measurement of the susceptibility, since the field (see below) is known to a much higher degree of accuracy.

A Magnion H-96 electromagnet and an HSR 1365 power supply with a special field-reversal unit provides fields from 0 to 15 000 G in conjunction with a model FFC-4 magnetic field regulator and a Rawson-Lush rotating-coil gaussmeter. The gaussmeter had been previously calibrated using nuclear magnetic-resonance techniques with both hydrogen and lithium probes. The field-set accuracy is within ±0.3% at 300 G and better than 0.15% at 10 000 G.

A PAR cryogenic temperature controller, along with the regulation of gas flow through the sample zone, was used to vary the temperature. When liquid helium was the cryogen, temperatures between 1.6 and 4.2 °K were achieved using standard pumping procedures along with the temperature controller, and temperatures between 4.2 and 90 °K were obtained using the proper combination of gas flow and heating. Using these methods, temperature stability was routinely maintained to better than ±0.01 °K. For temperatures in the region 77–300 °K, liquid nitrogen was used as the cryogen, and temperatures in this region were obtained with the above-mentioned techniques. However, in this region the required temperature stabilization was achieved only by a much more critical regulation of the gas flow and the administration of heat.

Temperature measurement and calibration

The temperature of the sample was measured using a GaAs diode in conjunction with a constant-current supply and a Dana Model 4700 4.5-place digital voltmeter.

A computer fit describing the voltage-temperature relationships of the GaAs thermometer over the range 1.6–290 °K was achieved using a polynomial of the form

$$\ln V = \sum_{j=0}^{n} A_j (\ln T)^j$$

and a commercially calibrated diode.[20] For maximum sensitivity and the best description of the temperature-voltage relationship, three regions of fit were chosen for the computer fit as described by Blakemore *et al.*[21] Hence polynomial fits have been used in the regions 1.6–30, 20–90, and 77–290 °K that at the same time afford a small overlap region between the regions of the fit. The fitted temperatures are well within the specifications stated by the manufacturer for the GaAs diode.

After the regression coefficients were computed for a given region and polynomial using a least-squares procedure, the input-voltage values were transformed to output-temperature values using a standard computer interpolation procedure.

RESULTS

A finely ground 0.0963-g sample of $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$ was encapsulated in a lucite sample holder, and data were collected

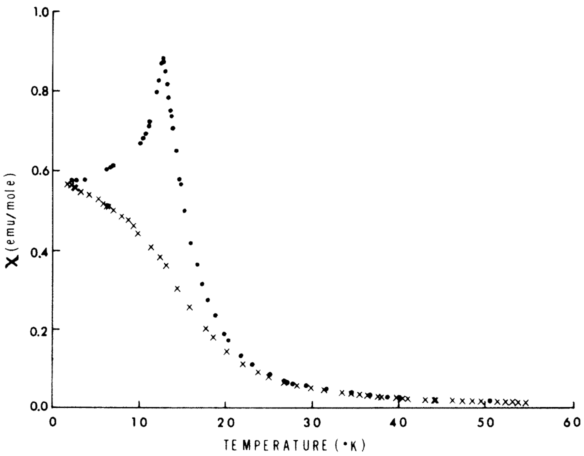

FIG. 3. Representation of the powder-susceptibility data collected at 500 (●) and 10 000 (×) G. Only data to 60 °K have been included.

from 1.6 to 160 °K at two field strengths, 500 and 10 000 G. From these results, as shown in Fig. 3, data collected above approximately 30 °K were independent of the field strength; as a result, for greater accuracy data above 40 °K were collected at 10 000 G exclusively.

Data were collected from 1.6 to 80 °K using liquid helium as the coolant, and from 77 to 160 °K using liquid nitrogen as the coolant. In the temperature region where the data overlapped, agreement was within 1%.

Diamagnetic corrections, which became quite significant above 77 °K, were accounted for by measuring the diamagnetism associated with the isomorphous Cd salt in the lucite sample holder. As can be seen in Fig. 3, when the data are collected at 10 000 G a featureless curve results which deviates significantly from Curie-Weiss behavior. However, when data are collected at 500 G the behavior below approximately 11.5 °K is characteristic of the powder susceptibility of an antiferromagnetic substance. This interpretation is further reinforced when the single-crystal susceptibilities are examined.

A rectangular-shaped single crystal weighing 0.0264 g was used for the measurements, which were made along the three crystallographic axes. The crystal was mounted on a lucite single-crystal holder with Apiezon *N* grease, and subsequently the orientation of the crystal on this sample holder was checked under a polarizing microscope. Relative orientations were confirmed by x rays. Since the magnetometer allows for a rotation of the sample by 360° in the plane of the magnetic field, the crystal was first placed on its (010) face and the sample holder aligned so that the field was parallel to *c*. A rotation of the crystal by 90° allowed measurements to be made along the *b* axis. The crystal was then rotated 90° on the sample holder and reoriented in the magnetic field, thereby allowing measurements to be made along the *a* crystallographic direction. A check was then possible for the measurements made along *b*. Because of the shape of the crystal, its orientation with respect to the sample holder was exact, and it is therefore estimated that the total orientation error does not exceed 1.5° for all three measurements.

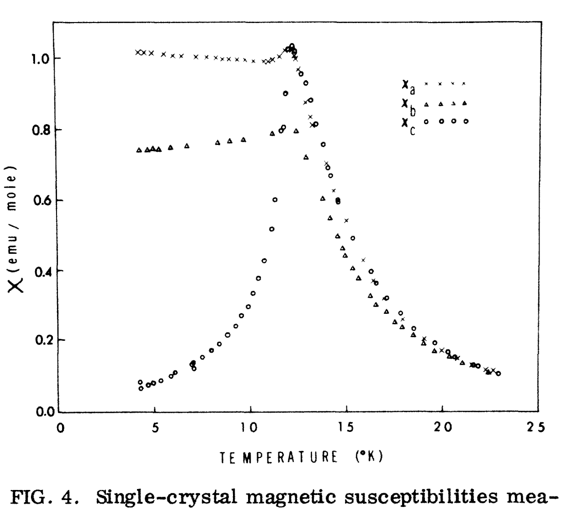

FIG. 4. Single-crystal magnetic susceptibilities measured along the three crystal axes. The data reflect the demagnetization corrections described in the text.

Data were collected at field strengths of 100 and 50 G, and little or no detectable field dependence was observed. Consequently, for greater accuracy data were collected at 500 G. The results of the measurements to 25 °K are shown in Fig. 4.

Because of the magnitude of the susceptibility close to the transition temperature, the data at 500 G were corrected for demagnetization effects. The standard formula

$$H_i = H_M - DM \tag{1}$$

was used to correct the measured susceptibilities, where H_M is the measuring field and M is the measured magnetization. The demagnetization factors used to correct the data along the *a*, *b*, and *c* axes are $4\pi D = 0.2$, 0.7, and 0.3, respectively. These factors have been calculated for an infinite rectangular bar magnetized transversely.[22] Although the correction is relatively insignificant for the *a* and *c* directions (less than 1.5%), the correction made perpendicular to the platelet, i.e., the *b* axis, amounts to 4%.

As can be seen in Fig. 4, the suggestion of a phase transition which appeared in the powder data is clearly revealed in the single-crystal data. Defining the temperature associated with the phase transition from the paramagnetic to antiferromagnetic state as the point of maximum positive slope along the preferred axis of magnetization,[23] the observed transition occurs at (11.87 ± 0.05)°K. Below this temperature, $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$ behaves as an antiferromagnet with orthorhombic anisotropy along two of the three crystal axes. The preferred axis corresponds to the *c* crystallographic axis, while the next preferred temperature independent direction is the *a* axis. The *b* axis corresponds to the least preferred orientation for the spins in the ordered phase. Although below the phase transition this material behaves as a typical orthorhombic antiferromagnet, above the transition the magnetic susceptibility of $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$ is hardly typical of an antiferromagnet—e.g., $CuF_2 \cdot 2H_2O$.[24] More precisely, the interaction which predominates above 11.87 °K is ferromagnetic in nature. This is revealed in the exceptionally large values of the susceptibility close to the transition, along with the field dependence of the susceptibility; i.e., decreasing the field increases the susceptibility.

EPR spectra were obtained with a Varian E-3 spectrometer operating at a frequency of 9.18 GHz (X band) with 100-kHz modulation along the crystal axes at liquid-nitrogen temperature; the results are $g_a = 2.166 \pm 0.005$, $g_b = 2.058 \pm 0.008$, and $g_c = 2.178 \pm 0.007$. The powder value is then equal to 2.134, and this value was used in the high-temperature susceptibility analysis unless otherwise specified. Although copper (II) compounds with this same two-dimensional network have axial spectra,[25] this appears not to be the case for $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$. Also, EPR linewidths on one- and two-dimensional magnetic systems are predicted by recently developed theory[26] to show a characteristic line-shape variation with rotation angle from the two-dimensional plane; however, our measurements on the pure material were inconclusive. (Further EPR work utilizing the Cd isomorph as a diamagnetic host lattice is in progress.)

The powder-susceptibility data from 110 to 160 °K were fitted to a Curie-Weiss expression of the form

$$\chi = C/(T-\theta), \tag{2}$$

where $C = Ng^2\mu_B^2/4k$. This expression yields the fitted parameters $g = 2.10 \pm 0.01$ and $\theta = (33.3 \pm 0.8)$ °K. While the fit is well within the experimental uncertainty over the entire temperature region, the resulting g value is somewhat lower than that determined by EPR. Perhaps improvement in the magnetic parameters would result if higher-temperature points could be obtained with sufficient accuracy. In this connection, it should be pointed out that there are significant deviations below 110 °K from the simple paramagnetic behavior predicted by the Curie-Weiss expression. Apparently this is a feature common to these nearly two-dimensional compounds since the series $[C_nH_{2n+1}]_2CuX_4$ displays the same behavior.[12,14] Compared to other systems of higher dimensionality, data from an extremely high-temperature range relative to the transition temperature are required in order for this expression to describe the magnetic behavior. Since θ in the molecular-field approximation is equal to $2J/k$ for a quadratic lattice and spin-$\frac{1}{2}$, a value of 16.7 °K for the exchange constant results from this fit.

More precise values for the exchange constant may be obtained by fitting the data from 30 to 110 °K to susceptibility expressions that have been derived from high-temperature series-expansion results for the quadratic lattice. Since the reliability of these methods increases dramatically with the number of terms in the series, the results of Baker *et al.*[27] for the two-dimensional Heisenberg model on a quadratic lattice have been used to fit the data from 30 to 110 °K. The series takes the following form:

$$\chi = (C/T)[1 + 2(J/kT) + 2(J/kT)^2 + \tfrac{4}{3}(J/kT)^3 + \cdots], \tag{3}$$

where C is the Curie constant. Because of the finite number of terms in the series, two methods were used to determine the sensitivity of the expression to the data for a given value of J/k and also to determine the temperature below which the series breaks down. The lowest appropriate temperature was established by truncating the series at seven terms rather than using the full ten terms. The fitted data were within the estimated experimental error using the full or truncated series down to 30 °K—i.e., where $J/kT > 0.6$. The sensitivity of the expression and the data to variations in the fitted exchange parameter was established by fitting the data from 30 to 110 °K and from 70 to 110 °K and observing the resulting variation in the exchange parameter. It was reasoned that any magnetic-field effects present in the lower-temperature region should cause a large variation in the exchange constant if field effects were important. In either temperature region, the identical value of (18.7 ± 0.2) °K resulted when the g value had been set equal to the EPR powder value. (There was no significant change in the g value if it was allowed to vary in the fitting procedure). The results of this fit are shown in Fig. 5.

When the series result derived by Dalton and

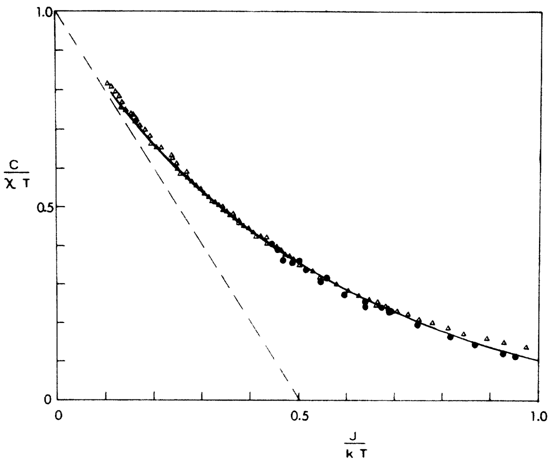

FIG. 5. Plot of the powder susceptibility and the fit (solid line) to the equation of Baker *et al.* for a two-dimensional Heisenberg ferromagnet. C is the Curie constant for $g = 2.134$ and $S = \frac{1}{2}$, while $J/k = 18.7$°K. The dashed line is the molecular-field prediction for a quadratic lattice. Triangles represent data collected at 10 kG while circles represent data collected at 500 G.

Wood[4] for the anisotropic Heisenberg model was applied to the data in the same temperature region, no difference in the quality of the fit could be detected between this model and Baker's results. The anisotropy parameter η was assigned the values $\eta = 0$ (Ising limit), $\eta = 0.75$, and $\eta = 1.0$ (Heisenberg limit) for the quadratic lattice. The values of $2J/k$ which resulted were 36.5 °K ($g = 2.21$), 42.0 °K ($g = 2.16$), and 48.7 °K ($g = 2.11$), respectively.

When the series results for the pure isotropic X-Y model[6] were applied, the fit was not satisfactory. Whether this is a manifestation of the fewer number of terms available for this series or, in fact, a clear reflection of the inadequacies of this model in this temperature range cannot be determined from this study.

DISCUSSION

From single-crystal magnetic-susceptibility measurements above and below T_N on $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$, it can be inferred that the electrons are aligned ferromagnetically within the a-c plane. The short-range ordering effects within this plane above T_N dominate the magnetic susceptibility down to the transition temperature, where the effects of the interlayer exchange and the anisotropy initiate the three-dimensional antiferromagnetic ordering which occurs below 11.87 °K. Below this temperature the ferromagnetically ordered layers are coupled antiferromagnetically along the b axis. The c axis is the preferred axis in the antiferromagnetic state, with the next preferred axis being the a axis. At least from dipole-dipole considerations, this ordering within layers is expected from the difference in the lengths of the crystallographic axes.

From effective field considerations, an exchange field equal to 5.1×10^5 G within the layer was deduced from the expression

$$H_E = 2z|J|S/g_{a-c}\mu_B , \tag{4}$$

where $S = \frac{1}{2}$, $z = 4$, $g_{a-c} = 2.172$, and the exchange constant is 18.7 °K (derived from the two-dimensional Heisenberg-series result).

As T_N is approached from high temperatures, the data become more anisotropic than that which can be ascribed to simple g-value anisotropy. Interestingly, there appears to be virtually no anisotropy in the a-c plane at the transition temperature and above. Presumably, interlayer exchange effects, as well as dipolar and exchange anisotropy, are beginning to be felt perpendicular to the plane at relatively high temperatures.

Because of the similarities in the crystal structures, it is possible to make comparisons between $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$ and the thoroughly studied $[C_2H_5NH_3]_2[CuCl_4]$.[12] The two compounds, as mentioned earlier, have identical two-dimensional layered structures, but have differences in the relative isolation of these layers. Despite the differences one might expect from the introduction of another chloride anion, which could provide a more facile exchange pathway for interlayer exchange, the two compounds are remarkably similar. A comparison of the various properties are made in Table I. The three-dimensional ordering clearly sets in at a higher temperature, and the absolute magnitude of the susceptibilities in the three directions are less in $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$, yet the same exchange constant fits both data sets using the same model along with the same spin configuration in the ordered state.

From differential-susceptibility measurements,[28] $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$ undergoes a spin-flop from the preferred c axis to the a axis which is comparable to that observed for $[C_2H_5NH_3]_2[CuCl_4]$. A more meaningful comparison of these two compounds will be possible when the various critical

TABLE I. A comparison of the magnetic and structural properties of the two copper compounds.

	$[C_2H_5NH_3]_2CuCl_4$	$[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$
Cu–Cl (1) (Å)	2.277	2.272
Cu–Cl (2) (Å)	2.285	2.276
Cu–Cl′ (2) (Å)	2.975	2.876
Cu–Cu (Å)	5.24	5.11
Space group	*Pbca*	*Pnma*
Cell parameters (Å):		
a	21.18	7.117
b	7.47	23.78
c	7.35	7.342
T_N (°K)	10.20	11.87
J/k (°K) [a]	18.6	18.7

[a] Derived series-expansion result of Baker *et al.* (Ref. 27).

fields are analyzed with respect to the differing amounts of intralayer anisotropy and interlayer exchange.

It has been a matter of experimental speculation[15] that the two-dimensional phase in the $S=\frac{1}{2}$ case is given by $T_c/\theta = 0.22$, where T_c is the observed transition temperature and θ is the molecular-field prediction for this temperature. The value of T_c/θ observed for $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$ when the high-temperature Curie-Weiss-derived θ is used is 0.36, and $T_c/\theta = 0.32$ if the value of 37.4 °K ($\theta = 2J/k$) from the high-temperature-series result is used instead. From a consideration of the temperature range used, as well as the fact that different values for the exchange constant result when different model Hamiltonians are used, it is felt that the Curie-Weiss value is a better reflection of the molecular-field predictions. What is apparent and perhaps surprising is that $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$ reflects the presence of the additional exchange pathway, and that its properties when close to T_N are more three-dimensional than two-dimensional relative to $[C_2H_5NH_3]_2CuCl_4$, even though the layers are separated by 11.8 Å in the former compound and 10.6 Å in the latter. On the other hand, T_c/θ is some 60% smaller than the values observed for typical three-dimensional ferromagnets, such as $K_2CuCl_4 \cdot 2H_2O$.[29]

In conclusion, it should be pointed out that there is a certain arbitrariness in the selection of an exchange constant. Although the high-temperature susceptibility, which deviates significantly from simple Curie-Weiss behavior, can be well described and is a sensitive gauge of the predominate exchange forces using a particular model, it must be pointed out that in terms of the quality of the resulting fits, no clear choice can be made between the available models. That is to say, the isotropic Heisenberg two-dimensional model describes the high-temperature data as well as the anisotropic Heisenberg model, although, obviously, different values for the calculated exchange constants result.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation through Grant No. GP-22887 and by the Materials Research Center of the University of North Carolina under Grant No. GH-33632 from the National Science Foundation.

---

[1] H. E. Stanley and T. A. Kaplan, Phys. Rev. Lett. 17, 913 (1966).

[2] N. D. Mermin and H. Wagner, Phys. Rev. Lett. 17, 1133 (1966).

[3] L. Onsager, Phys. Rev. 65, 117 (1944).

[4] N. W. Dalton and D. W. Wood, Proc. Phys. Soc. Lond. 90, 459 (1967); D. W. Wood and N. W. Dalton, J. Phys. C 5, 1675 (1972).

[5] T. Oguchi, J. Phys. Soc. Jap. 30, 988 (1971).

[6] T. Ishikawa and T. Oguchi, J. Phys. Soc. Jap. 31, 1021 (1971).

[7] D. D. Betts, C. J. Elliott, and R. V. Ditzian, Can. J. Phys. 49, 1327 (1971).

[8] M. E. Lines, Phys. Rev. B 3, 1749 (1971).

[9] J. M. Kosterlitz and D. J. Thouless, J. Phys. C 6, 1181 (1973).

[10] M. E. Fisher and D. Jasnow, Phys. Rev. B 3, 907 (1971).

[11] K. Yamaji and J. Kondo, J. Phys. Soc. Jap. 35, 25 (1973).

[12] L. J. De Jongh, W. D. Van Amstel, and A. R. Miedema, Physica (Utr.) 58, 277 (1972).

[13] J. H. P. Colpa, Physica (Utr.) 57, 347 (1972).

[14] L. J. De Jongh and W. D. Van Amstel, J. Phys. Suppl. 32, 880 (1971).

[15] P. Bloembergen, K. G. Tan, F. H. J. Lefevre, and A. H. M. Bleyendaal, J. Phys. Suppl. 32, 879 (1971).

[16] H. B. Jonassen, T. B. Crumpler, T. D. O'Brien, J. Am. Chem. Soc 67, 1709 (1945).

[17] G. L. Ferguson and B. Zaslow, Acta Crystallogr. B27, 849 (1971); B. Zaslow and G. L. Ferguson, Chem. Commun. 822 (1967).

[18] H. St. Räde, J. Phys. Chem. 77, 424 (1973).

[19] F. R. McKim and W. P. Wolf, J. Sci. Instrum. 34, 64 (1957).

[20] Type TG-100FPA (special), No. 4277, Lake Shore Cryotronics, Eden, N. Y.

[21] J. S. Blakemore, J. Winstel, and R. V. Edwards, Rev. Sci. Instrum. 41, 835 (1970).

[22] W. F. Brown, Jr., in *Magnetostatic Principles in Ferromagnetism*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1962).

[23] M. E. Fisher, Philos. Mag. 7, 1731 (1962).

[24] S. Tazawa, K. Nagata, and M. Date, J. Phys. Soc. Jap. 20, 181 (1965).

[25] F. Furlani, A. Sgamellotti, F. Magrini, and D. Cordischi, J. Mol. Spectrosc. 24, 270 (1967); R. D. Willet, O. L. Liles, Jr., and C. Michelson, Inorg. Chem. 6, 1885 (1967).

[26] M. J. Hennessy, C. D. McElwee, and P. M. Richards, Phys. Rev. B 7, 930 (1973).

[27] G. A. Baker, H. E. Gilbert, J. Eve, and G. S. Rushbrooke, Phys. Lett. A 25, 207 (1967).

[28] D. B. Losee and W. E. Hatfield (unpublished).

[29] A. R. Miedema, H. Van Kempen, and W. S. Huiskamp, Physica (Utr.) 29, 1266 (1963).