

## Exchange-Energy Constants in Some $S = \frac{1}{2}$ Two-Dimensional Heisenberg Ferromagnets\*†

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Several of the ferromagnetic two-dimensional magnetic structures similar to  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  have been studied by electron-paramagnetic resonance (EPR) methods and also by measuring magnetic susceptibility as a function of temperature, in order to determine the exchange-energy constants. A linear temperature dependence of the EPR linewidths shows (after Castner and Seehra) that the Dzialoshinsky-Moriya antisymmetric exchange interaction  $\vec{D}_{ij} \cdot \vec{S}_i \times \vec{S}_j$  must be included with the usual symmetric terms in the calculation of the moments. These compounds indicate an "intermediate" case where the antisymmetric exchange term is comparable in magnitude to the dipole-dipole energy. The values of the isotropic exchange energy  $J$  are derived by fitting the susceptibility data to a high-temperature expansion of the susceptibility with the leading contribution of  $\vec{D}$  included in the expansion. Values of  $J \approx 10 \text{ cm}^{-1}$  are found with  $\vec{D}$  more than twenty-times smaller. Additional comments are made about the thermochroic transition exhibited by these substances.

### I. INTRODUCTION

Recently, a number of compounds have been found which contain two-dimensional magnetic sublattices. Principally, these have been the  $(\text{C}_n\text{H}_{2n-1}\text{NH}_3)_2\text{CuCl}_4$  compounds for which the ferromagnetic transition temperature has been studied by deJongh *et al.*<sup>1</sup> Interest in these "two-dimensional" magnetic structures increased when Mermin and Wagner rigorously proved that there cannot be a spontaneous magnetization for a Heisenberg magnet in one or two dimensions.<sup>2</sup> They point out, however, that the results are inconclusive when some anisotropy is present. About the same time Stanley and Kaplan showed that a divergence in the susceptibility could occur in two-dimensional systems at finite temperature.<sup>3</sup> Since a number of the compounds mentioned above have shown spontaneous magnetization, this is interpreted to mean that the third dimension of the real crystal enables magnetization to appear, but that the actual corrections to the two-dimensional calculations are small.<sup>4</sup> Significant work has progressed on various forms of copper formate, for example, which show two-dimensional qualities.<sup>5,6</sup> The present work measures the exchange energies of the  $\text{CuCl}_4$  series of compounds mentioned above as well as two of the similar series of  $\text{CuCl}_2\text{Br}_2$ . These are of interest as the magnetic ions lie in a plane with only a single intervening anion through which exchange takes place. The planes are separated by nonexchange organic material.

A difficulty with some of these structures pointed out by Willett<sup>7</sup> is that a transition temperature ex-

ists above that of the onset of magnetization such that a crystal-structure change obtains. This transition, called thermochroism, is usually seen as a change in color as the crystal is cooled. The compounds of  $\text{CuCl}_2\text{Br}_2$  recently developed by Willett were originally thought not to have this thermochroic property, however, the electron-paramagnetic resonance (EPR) clearly shows a linewidth behavior similar to that of the  $\text{CuCl}_4$  species. The series of  $\text{CuCl}_2\text{Br}_2$  differ from that of  $\text{CuCl}_4$  only in the off-plane constituents as described in Sec. II.

The EPR data exhibit the expected extreme exchange narrowing but they also exhibit a significant range of linear temperature dependence. Seehra and Castner<sup>8</sup> have recently shown that such a temperature dependence arises from a phonon modulation of the antisymmetric exchange energy introduced by Dzialoshinsky<sup>9</sup> and Moriya.<sup>10</sup> Section III indicates the appropriate EPR linewidth calculation for the  $\text{CuCl}_4$  and  $\text{CuCl}_2\text{Br}_2$  compounds and shows that these are cases where both the dipole-dipole and antisymmetric-exchange terms should be kept in the second-moment contribution. Section IV uses a high-temperature series expansion of the susceptibility with the antisymmetric term included to interpret susceptibility data obtained by magnetometer methods. The resulting values of the symmetric and antisymmetric exchange energies are presented.

### II. CRYSTAL STRUCTURE

The crystal structures of methylammonium (MA) dichloro-dibromocuprate  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$ <sup>11</sup> and

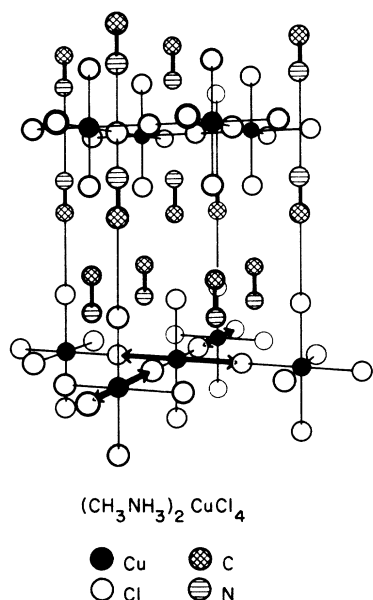


FIG. 1. Schematic of the structure of methylammonium tetrachlorocuprate. The Cu (solid black) form a plane with Cl (open circles) between each Cu. The arrows indicate the long axis of the distorted Cl octahedron. The planes are separated by C (shaded circles) and N (dashed circles). The structure for (MA)CuCl<sub>2</sub>Br<sub>2</sub> is similar except that the off-plane Cl are replaced by Br.

methylammonium (MA) tetrachlorocuprate (CH<sub>3</sub>NH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub><sup>12</sup> are well known and consist of two-dimensional layers of CuCl<sub>2</sub> anions with the layers separated by CH<sub>3</sub>NH<sub>3</sub> groups. The Cu-Cl bonds lie in the plane with either the Cu-Br bonds or Cu-Cl bonds perpendicular to the plane such that the CuCl<sub>2</sub>Br<sub>2</sub> or the CuCl<sub>4</sub> form a distorted octahedral site for the copper. This is illustrated schematically in Fig. 1. The arrangement of the octahedra are such that the long axis (*z* axis) of one site is perpendicular to that of the next site so that each Cu-Cl-Cu bond is the *z* axis of one of the Cu octahedra and the *x* axis of the next. The in-plane Cu-Cl-Cu bond is nearly linear at room temperature and forms a bridge for superexchange to take place. The bond-length distance for (MA)CuCl<sub>2</sub>Br<sub>2</sub> is 5.191 Å and for (MA)CuCl<sub>4</sub> is 5.252 Å. The distance between planes is about 10 Å. The structure of ethylammonium (EA)CuCl<sub>4</sub> [(C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub>] and *n*-propylammonium (*n*PA)CuCl<sub>2</sub>Br<sub>2</sub> [(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)<sub>2</sub>CuCl<sub>2</sub>Br<sub>2</sub>], as well as (*n*PA)CuCl<sub>4</sub> appear to be similar to the planar structure of (MA)CuCl<sub>4</sub> and (MA)CuCl<sub>2</sub>Br<sub>2</sub> with the appropriate number of additional CH<sub>2</sub> chains between planes. Each CH<sub>2</sub> adds about 1.5 Å to the interplanar separation.

### III. EPR LINEWIDTHS

An appropriate spin Hamiltonian for the Cu<sup>2+</sup> sys-

tem is

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{DD} + \mathcal{H}_E + \mathcal{H}_{DM}, \quad (1)$$

where  $\mathcal{H}_Z$  and  $\mathcal{H}_{DD}$  are the usual Zeeman and dipole-dipole terms,

$$\mathcal{H}_E = -2J \sum_{ij} \vec{S}_i \cdot \vec{S}_j \quad (2)$$

is the isotropic-symmetric exchange term with only nearest-neighbor interactions considered and all assumed equivalent, and

$$\mathcal{H}_{DM} = \sum_{ij} \vec{D}_{ij} \cdot \vec{S}_i \times \vec{S}_j \quad (3)$$

is the antisymmetric exchange term introduced by Dzialoshinsky and Moriya.

It was the symmetric term of Eq. (2) which Van Vleck<sup>13</sup> used to explain the anomalously narrow EPR linewidths by showing that its inclusion into the calculation of the second and fourth moments sharply reduces the calculated linewidth. His calculations were simplified by using only the diagonal matrix elements of the dipole-dipole Hamiltonian. However, when the exchange frequency  $\omega_E = J/\hbar = g\mu_B H_E/\hbar$  is much greater than the experimental EPR frequency  $\omega_0 = g\mu_B H_0/\hbar$  the off-diagonal elements contribute to additional broadening. This latter contribution is called the “ $\frac{10}{9}$  effect” and is treated in detail by Anderson and Weiss<sup>14</sup> and Tomita.<sup>15</sup> In this case the exchange energy is given by<sup>16</sup>

$$J = 1.31 g\mu_B M_{2DD} / \Delta H, \quad (4)$$

where  $\Delta H$  is the linewidth measured between points of maximum slope assuming a Lorentzian line shape and

$$M_{2DD} = \frac{3}{4} S(S+1) g^4 \mu_B^4 \sum_j r_{ij}^{-6} (3 \cos^2 \theta_{ij} - 1)^2 \quad (5)$$

is the second-moment contribution to the line shape when  $\mathcal{H}_{DM}$  is not included.

A difficulty arises in attempting to calculate an exchange energy from the linewidths as they are strong functions of temperature. These temperature dependences are shown in Figs. 2 and 3 and exhibit three definite regions of behavior. The uppermost region shows very steep increase in width as temperature increases while the temperature dependence in the middle region appears to be linear. The definite knee at about 210 °K in the CuCl<sub>2</sub>Br<sub>2</sub> series is probably the exhibition of thermochroism not previously thought to exist in these crystals. It is likely that a puckering of the Cu-Cl-Cu bonds occurs bringing the Cl out of the plane which reduces the strength of the superexchange interaction. The lowest region is thought to indicate the onset of long-range ordering. It is the middle range in which the interest lies. Castner and Seehra have provided us with the method

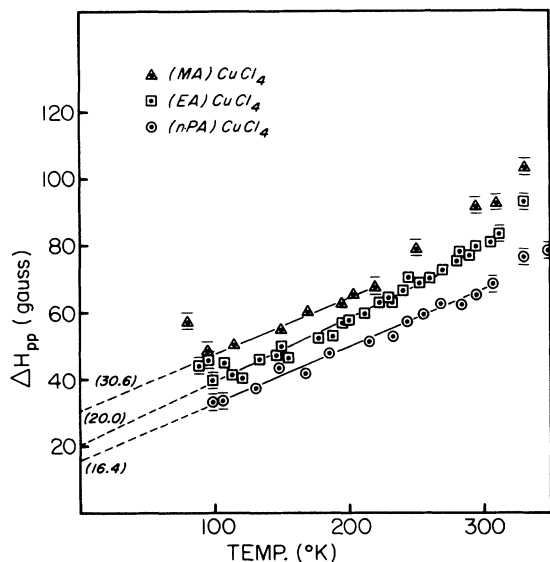


FIG. 2. Peak-to-peak EPR linewidths as a function of temperature for the  $\text{CuCl}_4$  series. The straight lines are the least-squares best fit of the data to determine the  $T=0$  intercept of  $\Delta H_{pp}$ . The value of the intercept is given in parentheses.

to proceed by showing that a phonon modulation of the Dzialoshinsky and Moriya antisymmetric exchange,  $\mathcal{K}_{DM}$  of Eq. (3), gives a linear temperature dependence<sup>8</sup> and they have furthermore provided the magnitude of this effect by including the  $\mathcal{K}_{DM}$  term in the second- and fourth-moment calculations of EPR linewidths.<sup>16</sup> Their work was applied to antiferromagnetic copper formate tetrahydrate but we shall use their results on the ferromagnetic tetrachloro cuprates and dichloro dibromo cuprates. They have essentially shown if the symmetry of the system is low enough so that an antisymmetric exchange is present, the linewidth study cannot yield a value of  $J$  alone, but rather yields a value for  $|\vec{D}|^2/J$ .

It is first necessary to use the symmetry rules of Moriya and Dzialoshinsky to determine if such an interaction can exist. Looking at the two-dimensional layer in Fig. 1 and noting that the in-plane chlorines are not midway between the nearest copper ions, Moriya's rules allow at least a contribution in the magnetic plane. Moriya's rules cannot be unambiguously applied here as the crystal structure is not exactly known in this temperature region but from the data it appears that the puckering probably puts the chlorine more nearly midway between the coppers thereby also reducing the effect of  $\mathcal{K}_{DM}$ . We choose the direction perpendicular to the plane for the  $z'$  axis,  $x'$  and  $y'$  being in the plane. It should be noted that in EPR studies the  $z$  direction is considered to be the long axis of the distorted octahedron which lies in the plane

and alternates directions at successive sites.

The symmetries for our samples are similar to that of copper formate so that under the assumption that  $J_{ij} \gg |\vec{D}_{ij}|$  and neglecting crystal-field terms, we can apply directly the results of Castner and Seehra. They show that the second moment is given by

$$M_2 \cong S(S+1) \left[ \frac{2}{3} (\mathcal{D}_y^2 + \mathcal{D}_z^2) + M_{2DD} \right], \quad (6)$$

and there are no cross terms between  $|\vec{D}|^2$  and  $M_{2DD}$ . They also calculate the contribution to the fourth moment which shows that the assumption of a Lorentzian times a simple exponential line shape is reasonable and gives

$$\Delta\nu_{1/2} \cong \frac{1}{2}\pi (M_2/Jh) \quad (7)$$

for the measured half-frequency at half-maximum.

The copper formate compounds showed  $|\vec{D}|^2 \gg M_{2DD}$  so that the dipole-dipole terms could be neglected. If the symmetry is high enough, that is if  $\vec{D}=0$ , then the resulting exchange is given by Eq. (4). Initial calculations for the  $\text{CuCl}_4$  and  $\text{CuCl}_2\text{Br}_2$  compounds of this study however, indicate that  $M_{2DD}$  is less than  $|\vec{D}|^2$  but not "much less than," therefore we have an intermediate case where both the usual  $M_{2DD}$  terms and the  $|\vec{D}|^2$  terms should be kept.

For the square, planar system Eqs. (4)–(7) lead to a value of the exchange-narrowed full linewidth of

$$\Delta H = (\pi/\sqrt{3}) \left( \frac{1}{3} |\vec{D}|^2 + M_{2DD} \right) / Jg\mu_B. \quad (8)$$

The linewidth used in Eq. (8) is that measured from

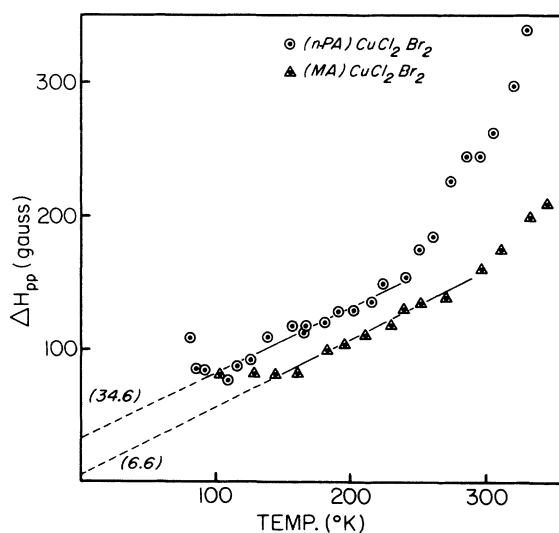


FIG. 3. Peak-to-peak EPR linewidths as a function of temperature for the  $\text{CuCl}_2\text{Br}_2$  series. The straight lines are the least-squares best fit of the data to determine the  $T=0$  intercept of  $\Delta H_{pp}$ . The value of the intercept is given in parentheses.

TABLE I. Room-temperature  $g$  values relative to the Cu plane.

	$g_{\parallel}$	$g_{\perp}$
(MA)CuCl <sub>2</sub> Br <sub>2</sub>	2.122 ± 0.006	2.035 ± 0.006
(nPA)CuCl <sub>2</sub> Br <sub>2</sub>	2.113 ± 0.006	2.051 ± 0.006
(MA)CuCl <sub>4</sub>	2.169 ± 0.003	2.054 ± 0.002 <sup>a</sup>
(EA)CuCl <sub>4</sub>	2.164 ± 0.003	2.053 ± 0.002 <sup>a</sup>
(nPA)CuCl <sub>4</sub>	2.160 ± 0.003	2.053 ± 0.002

<sup>a</sup>SeeRef. 18.

the extrapolation of the region of linear temperature to  $T=0$  (see Figs. 2 and 3). We assume  $|\vec{D}|^2 \approx \frac{3}{2}(\mathcal{D}_y^2 + \mathcal{D}_z^2)$  and both  $|\vec{D}|^2$  and  $M_{2DD}$  are represented in units of  $\text{erg}^2$ .

Table I gives the X-band EPR  $g$  values measured at room temperature including those compounds already measured.<sup>17</sup>  $g_{\parallel}$  and  $g_{\perp}$  are those  $g$  values when the external magnetic field is parallel and perpendicular to the magnetic plane, respectively.<sup>18</sup> The straight lines shown in Figs. 2 and 3 provide a measurement of the  $T=0$  intercept of  $\Delta H(T)$  and are found by a least-squares fit of the EPR data using the apparent linear region.

#### IV. MAGNETIC SUSCEPTIBILITY

The magnetic interaction for these compounds is assumed to be isotropic since to date the experimental sensitivity has not been great enough to detect anisotropy. If we can assume that the magnetic ions form a simple square lattice within a layer and if we ignore the interactions between layers using only the isotropic exchange interaction of Eq. (2) then after Rushbrooke and Wood,<sup>19</sup> a nearest-neighbor Heisenberg model leads to a high-temperature series expansion for the magnetic susceptibility  $\chi$ <sup>20</sup>

$$\begin{aligned} \chi T/C = & 1 + 2(J/kT) + 2(J/kT)^2(1 - \frac{1}{2}\Lambda^2) \\ & + \frac{4}{3}(J/kT)^3(1 - 6\Lambda^2) \\ & + \frac{13}{12}(J/kT)^4(1 - 26.8\Lambda^2 + 0.616\Lambda^4) \\ & + \frac{71}{80}(J/kT)^5(1 - 57.7\Lambda^2 + 9.58\Lambda^4) \\ & + \frac{387}{720}(J/kT)^6(1 - 23.6\Lambda^2 + 15.9\Lambda^4 - 0.741\Lambda^6) \\ & + \dots, \quad (9) \end{aligned}$$

where  $C$  is the Curie constant,  $H$  is the applied magnetic field,  $\Lambda = (g\mu_B H)/J$ , and  $\mu_B$  is the Bohr magneton.

Since it is apparent that the existence of the antisymmetric term plays an important role in the EPR analysis, we include it in the calculation for the high-temperature susceptibility expansion above. Repeating the procedures of Rushbrooke and Wood, and including the interaction of Eq. (3) we get a leading  $\mathcal{D}$ -dependent term in the suscep-

tibility of

$$(\chi T/C)_{DM} = -(\frac{1}{3}\mathcal{D}_x^2 + \frac{1}{3}\mathcal{D}_y^2 + \frac{1}{4}\mathcal{D}_z^2)/(kT)^2, \quad (10)$$

which will be a correction to the third term on the right-hand side of Eq. (9). It is obvious that the correction is small as even Moriya's estimate of  $\mathcal{D} \approx (\Delta g/g)J$  gives a correction of only 10% or so in that term and therefore only a few percent in the susceptibility. As shown before,<sup>6</sup> the experimental value of  $\mathcal{D}$  is 20 times or so smaller than  $J$  making the susceptibility somewhat insensitive to the antisymmetric exchange. That it should have such a strong effect in EPR is reasonable as the resonant experiment samples the individual spin environment and therefore detects departure from  $H_0$  at the site owing to internal interactions, while the susceptibility experiment measures macroscopic magnetization.

The magnetic susceptibility measurements were made using a Foner-type vibrating-sample magnetometer in a field of 8000 G. Because of small single-crystal size, a randomly oriented polycrystal (powder) sample was used. The experimental data are shown in Figs. 4 and 5. By plotting  $1/\chi$  as a function of temperature, it is clear that there is a definite region for which the systems exhibit paramagnetism. The straight lines drawn through

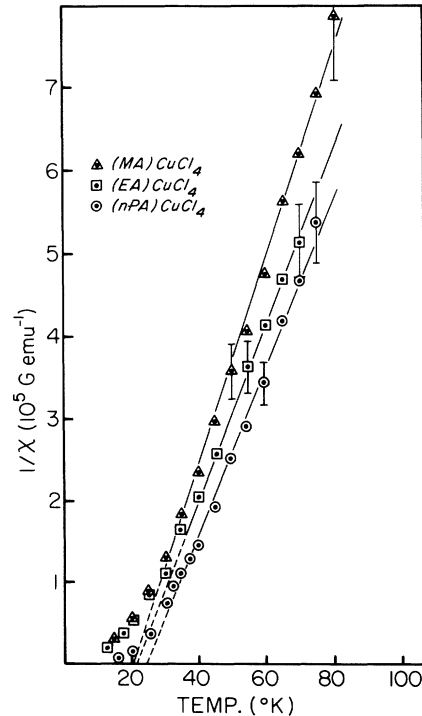


FIG. 4.  $1/\chi$  as a function of temperature for the CuCl<sub>4</sub> series. The straight lines indicate the extrapolation of the paramagnetic region to give the Curie temperature  $\Theta$ . All data normalized to 90 mg.

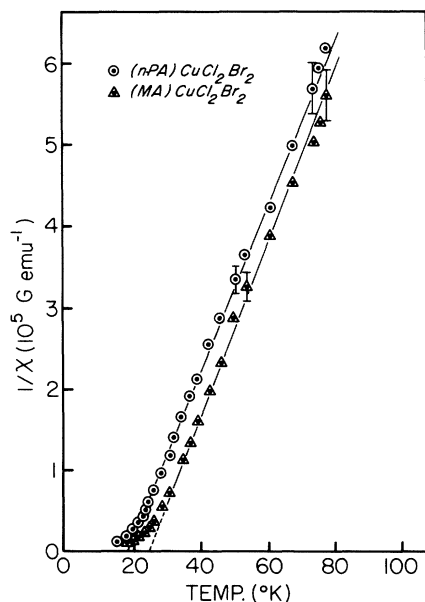


FIG. 5.  $1/\chi$  as a function of temperature for the  $\text{CuCl}_2\text{Br}_2$  series. The straight lines indicate the extrapolation of the paramagnetic region to give the Curie temperature  $\Theta$ . All data normalized to 90 mg.

the data represent a reasonable fit of the data points and make possible estimates of relative Curie constants for the compounds. Extrapolating this linear behavior gives the paramagnetic transition temperature or the Weiss temperature  $\Theta$ , values of which are listed in Table II. The vertical error bars in Fig. 2 are about  $\pm 5\%$  of the absolute value for all points shown. This means the data are not good for temperatures near  $80^\circ\text{K}$  but that the curvature, which suggests the onset of the ordering process, is well defined.

It was not necessary to include terms higher than  $(J/kT)^5$  for the fitting of the  $1/\chi$  data to Eq. (9) as such corrections fall within experimental error. Magnetic field corrections were included in the calculations, although they are apparently not important since  $H = 8 \text{ kG}$ ,  $g\mu_B H/hc = 0.744 \text{ cm}^{-1}$  giving  $\Lambda^2 \approx 1.6 \times 10^{-3}$ .

## V. DISCUSSION

The best fits from the EPR and susceptibility data for the determination of the energies  $J$  and  $|\vec{D}|$  as determined from Eqs. (8)–(10) are given in Table II. For an additional comparison of  $J$ , one may expand the simple Curie-Weiss law  $\chi = (C/T)[1 - (\Theta/T)]^{-1}$  and compare to the first two terms of the high-temperature series expansion in Eq. (9). Then

$$(C/T)(1 + 2J/kT + \dots) = (C/T)(1 + \Theta/T + \dots) \quad (11)$$

gives  $J = \frac{1}{2}k\Theta$ . For our case of  $S = \frac{1}{2}$  with four nearest neighbors, this value of  $J$  agrees exactly with that derived from a Weiss molecular-field calculation, viz.,  $J = 3k\Theta/2nS(S+1)$ , where  $n$  is the number of the nearest neighbors.<sup>21</sup> The values for  $J$  calculated in this manner are also included in Table II and it can be seen that they are in qualitative agreement except for the  $\text{CuCl}_2\text{Br}_2$  series where they are low by about a factor of 2.

The lack of knowledge of the specific crystal structure prevents an exact application of Moriya's symmetry rules but it is evident from room-temperature structures that the antisymmetric term must be included in the Hamiltonian. Also if this term is neglected, there is no way to reconcile the EPR and susceptibility data, i. e., a value of  $J$  an order of magnitude too small to satisfy susceptibility data would be necessary to explain the EPR linewidths. This low value of  $J$  is not consistent with this data even if a three-dimensional high-temperature series expansion for  $1/\chi$  is used. Finally, the linear temperature dependence of the linewidths indicates that the antisymmetric exchange term is important in the ferromagnetic case as previously suggested.<sup>8</sup>

Using the transition temperatures  $T_c$  measured by deJongh *et al.*<sup>1</sup> together with the values of  $J$  shown in Table II, the ratios of  $J/kT_c$  for the  $\text{CuCl}_4$  series are from 1.20 to  $1.77 \pm 0.2$ , in at least qualitative agreement with their work. The values of  $\mathcal{D}/J$  are about a factor of 5 lower than predicted by Moriya.<sup>10</sup>

*Note added in proof.* Since this paper was written

TABLE II. Values of the exchange constants as determined from susceptibility and EPR measurements. The last column is the isotropic exchange constant as determined from the Curie temperature. Entries without errors indicated are assumed to have same error as entry immediately above.

Compound	$J(\text{cm}^{-1})$ from susceptibility	$ \vec{D} (\text{cm}^{-1})$	$ \vec{D} /J$	$\Theta$ ( $^\circ\text{K}$ )	$J = \frac{k\Theta}{2hc}$ ( $\text{cm}^{-1}$ )
(MA) $\text{CuCl}_2\text{Br}_2$	$16.7 \pm 2.0$	$0.060 \pm 0.015$	0.0036	$25 \pm 2$	$8.7 \pm 2$
( $\bar{n}$ PA) $\text{CuCl}_2\text{Br}_2$	11.8	$0.123 \pm 0.003$	0.014	18	6.3
(MA) $\text{CuCl}_4$	8.5	0.101	0.012	$20 \pm 3$	7.0
(EA) $\text{CuCl}_4$	8.5	0.101	0.012	22	7.7
( $\bar{n}$ PA) $\text{CuCl}_4$	9.8	0.087	0.0087	25	8.7

it has come to the attention of the authors that deJongh and van Amstel have measured the values of  $J$  in the  $(C_nH_{2n-1}NH_3)_2CuCl_4$  series for  $n=1-6$  and  $n=10$ . Their values, corrected for diamagnetism, are approximately 50% higher than ours.<sup>22</sup>

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<sup>18</sup>Error bars shown in Fig. 2 and 3 are significantly larger than would normally be expected for measurements of these widths owing to an apparent instability in the crystal structure. That is, the crystals are history dependent and have a double EPR line under conditions which seem to vary. The possibility that this double spectrum obtains because there is a breaking up of the magnetic plane into exchange-narrowed one-dimensional chains is being further studied. This is related to the thermochroic property.

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