tained, although in this case the cone angles are no longer close to the theoretical values. The object of the above calculation is to suggest that small perturbations of the ferrimagnetic spiral may well be expected to bring the model into even closer agreement with experiment. A detailed comparison will require not only a further refinement of the theory, but also the collection of more complete experimental data from single crystals.

ACKNOWLEDGMENTS

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Theory of Exchange Resonance in Antiferromagnetic $CuCl_2 \cdot 2H_2O$†

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The low crystal symmetry of antiferromagnetic $CuCl_2 \cdot 2H_2O$ allows an antisymmetric, anisotropic, superexchange interaction (Moriya interaction) of the form $\mathbf{D}_{12}\cdot[\mathbf{S}_1\times\mathbf{S}_2]$ between corner and base-center copper ions. The classical magnetic-resonance frequencies and spin-wave frequencies have been derived for a four-sublattice model from a spin Hamiltonian consisting of nearest- and next-nearest-neighbor isotropic superexchange interactions, the Moriya interaction, and orthorhombic anisotropy energy. A set of high-frequency exchange modes was obtained in addition to the usual antiferromagnetic resonance modes. The former are characterized by the beating in opposition of ferromagnetic sublattices which would be degenerate in the absence of the Moriya interaction. The exchange frequencies are proportional to the geometric average of the ferromagnetic and antiferromagnetic exchange fields and are an order of magnitude larger than the antiferromagnetic frequencies. A resonance absorption experiment is proposed to detect the exchange modes; zero field magnetic resonance is expected at about 0.7 mm.

I. INTRODUCTION

It is well known[1,2] that the presence of anisotropy has a marked effect on the properties of antiferromagnets. Existing theories[3–6] of antiferromagnetic resonance in copper chloride dihydrate have incorporated, in a phenomenological form, the orthorhombic anisotropy energy arising from the anisotropy of the g factor and from the magnetic dipole and pseudodipole interactions. This latter interaction, a combined effect of spin-orbit coupling and exchange interaction, is of second order in the spin-orbit coupling and is symmetric in the interchange of the two spins. Recently Moriya[7] proposed a new mechanism of anisotropic superexchange interaction of the form

$$(\mathcal{H}_m)_{ij}=\mathbf{D}_{ij}\cdot[\mathbf{S}_i\times\mathbf{S}_j], \qquad (1)$$

which is linear in the spin-orbit coupling, antisymmetric in the interchange of the two spins, and generally an order of magnitude larger than the pseudodipole coupling. According to Moriya the presence of this interaction in $CuCl_2 \cdot 2H_2O$ results in a canted equilibrium spin configuration.

The effect of the canted spin arrangement in copper chloride is to introduce additional normal modes of vibration in which originally degenerate ferromagnetic sublattices (i.e., degenerate in the absence of the Moriya interaction) beat against each other with a relatively high frequency proportional to the geometric mean of the exchange fields involved. Some of these high-frequency modes exhibit a net magnetization and may be excited by an rf field.

It is the purpose of this paper to derive the magnetic resonance conditions and spin wave dispersion relations for the exchange modes in antiferromagnetic $CuCl_2 \cdot 2H_2O$ and to propose a resonance absorption experiment to detect them. The crystal structure and symmetry elements of $CuCl_2 \cdot 2H_2O$, the spin superstructure, the Moriya interaction, and the four-sublattice model are described in the following section. In Sec. III the resonance frequencies and normal modes of the four-sublattice model are derived from the classical equations of motion at 0°K. An applied field is included in the equations of motion in Sec. IV, and its effect on each of the resonances is discussed. The present theoretical results are compared with experiment and previous

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theory in Sec. V and numerical values for the exchange and anisotropy fields are obtained. The spin wave spectrum for small **k** is presented in Sec. VI and in Sec. VII a resonance absorption experiment is proposed to detect the exchange modes.

II. THE MORIYA INTERACTION IN $CuCl_2 \cdot 2H_2O$

The crystal of $CuCl_2 \cdot 2H_2O$ is orthorhombic with lattice parameters $a = 7.38$ A, $b = 8.04$ A, and $c = 3.72$ A. There are two copper ions in the chemical unit cell at (0,0,0) and $(\frac{1}{2},\frac{1}{2},0)$. Below the Néel temperature of 4.33°K, the spins of the Cu^{2+} ions take the antiferromagnetic arrangement determined by the proton resonance absorption experiment of Poulis and Hardeman.[8] Within the limits of the experiment, all the electron spins in a given *ab* plane are parallel to each other and antiparallel to the spins in the *ab* planes immediately above and below. The direction of easy magnetization is the *a* axis. Also in the unit cell are four water molecules at $(0, \pm u, 0)$ and $(\frac{1}{2}, \frac{1}{2} \pm u, 0)$ with $u = 0.25$, and four chlorine ions at $(\pm u, 0, \pm v)$ and $(\frac{1}{2} \pm u, \frac{1}{2}, \pm v)$ with $v = 0.37$. The copper ions are subjected to an approximately orthorhombic crystalline field which has different orientations for the corner and base-center ions. One of the principal axes of the field coincides with the *b* axis of the crystal while the other two axes are rotated about the *b* axis away from the *a* and *c* axes by an angle $+\beta_0$ for the corner ions and $-\beta_0$ for the base-center ions. Thus the two magnetic ions in a chemical cell are not crystallographically equivalent. The crystal structure and symmetry elements of $CuCl_2 \cdot 2H_2O$ are shown in Fig. 1.

The interaction expressed by (1) is the antisymmetric part of the general bilinear spin-spin interaction. In crystals of high symmetry this interaction between two magnetic ions vanishes, e.g., when there is a center of inversion midway between the two ions. This is easily seen from the fact that if there is inversion symmetry between ions 1 and 2, then $\mathbf{D}_{12} = \mathbf{D}_{21}$, whereas it is true in general that since $\mathbf{D}_{12} \cdot [\mathbf{S}_1 \times \mathbf{S}_2] = \mathbf{D}_{21} \cdot [\mathbf{S}_2 \times \mathbf{S}_1]$, we have $\mathbf{D}_{12} = -\mathbf{D}_{21}$. Lower crystal symmetry elements impose less restrictive conditions on **D**. Since D is of order $\Delta g/g$ times the isotropic superexchange integral, where g is the gyromagnetic ratio, while the magnetic dipole and pseudo-dipole terms are another factor of $(\Delta g/g)$ smaller, this antisymmetric part of the anisotropic superexchange interaction may provide the largest contribution to the anisotropy energy when the crystal symmetry is sufficiently low.

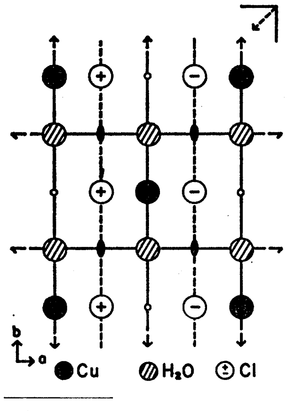

FIG. 1. Crystal structure and symmetry elements of $CuCl_2 \cdot 2H_2O$ (ion sizes not to scale).

There are inversion centers between all pairs of corner (base-center) copper ions in copper chloride, so the Moriya interaction vanishes between these pairs. However, between corner and base-center ions the highest symmetry element is a twofold rotation axis perpendicular to the line joining the ions. This symmetry restricts the Moriya vector to the *ab* plane, i.e., $\mathbf{D} = (D_a, D_b, 0)$. There is no *a priori* reason for either D_a or D_b to vanish and in fact they are of the same order of magnitude. However, D_a may be neglected as shown by the following argument.

In the absence of a Moriya interaction the ground state of a ferromagnetic or antiferromagnetic interaction between two spins is one in which the spins are colinear. The introduction of an antisymmetric coupling causes the two spins to rotate in opposite directions in the plane perpendicular to the Moriya vector. Starting with a spin Hamiltonian consisting of isotropic superexchange and Moriya interactions, the equilibrium position is described by

$$\tan 2\theta = D/J \approx (g-2)/g, \tag{2}$$

where 2θ is the angle between spins, D is the magnitude of the Moriya vector, and J is the exchange integral, defined as positive for ferromagnetic and negative for antiferromagnetic interactions. If we assume that the spins in copper chloride are initially held to the *a* axis by a small anisotropy field, then by turning on the Moriya interaction the following perpendicular spin components are induced:

$$\begin{aligned} S_b &\approx (D_a D_b / 4J^2) S_a, \\ S_c &\approx (D_b / 2J) S_a. \end{aligned} \tag{3}$$

Since $(g-2)g \approx 0.1$ in $CuCl_2 \cdot 2H_2O$, the spin canting caused by D_a is an order of magnitude smaller than that caused by D_b and the contribution to the energy from D_a is two orders of magnitude smaller than that from D_b. Thus D_a has only a negligible effect and in ignoring it we gain the advantage of a reduction in the number of sublattices needed to describe the magnetization. A four-sublattice model as shown in Fig. 2 seems reasonable. The magnetic unit cell contains two chemical unit cells oriented in the *c* direction as indicated by the experiment of Poulis and Hardeman.[8] It should be noted that the *a priori* choice of a four-sublattice model requires that the net effect of D_a be zero, as was pointed out by Moriya. (What happens is that the D_a contributions to the energy of a pair $\mathbf{S}_i$, $\mathbf{S}_j$ are cancelled by the contributions of a pair $\mathbf{S}_i$, $\mathbf{S}_k$ if $\mathbf{S}_j$ and $\mathbf{S}_k$ are required to be parallel.)

The four sublattice model shown in Fig. 2 is one in

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[8] N. J. Poulis and G. E. G. Hardeman, Physica **18**, 201 (1952).

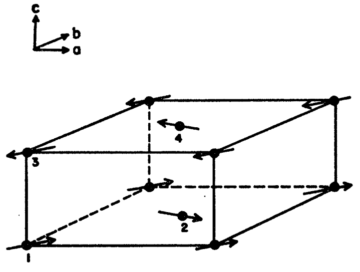

FIG. 2. Moriya's four-sublattice model of $CuCl_2 \cdot 2H_2O$. All spins are in the *ac* plane.

which all spins on a given sublattice are parallel. The nearest neighbors of an ion on sublattice 1 (2) are on sublattice 3 (4), while sublattices 1 and 2 (3 and 4) contain only mutually next-nearest-neighbor ions. The interaction between nearest neighbors is antiferromagnetic and that between next-nearest neighbors is ferromagnetic. This latter interaction must be included, not only because we want to investigate the effect of the Moriya interaction which is between next-nearest neighbors, but also because without this interaction the crystal would behave as a set of independent, linear chains running along the *c* axis, which Oguchi[9] and Marshall[10] have shown cannot be antiferromagnetic.

III. CLASSICAL CALCULATION AT 0°K; ZERO FIELD RESONANCE

For the dynamic case we use the equation of motion which states that the rate of change of angular momentum of a system is equal to the torque acting on the magnetization vector of the system and apply it to each of the four sublattices:

$$d\mathbf{M}_i/dt=\gamma_0\mathbf{M}_i\times\mathbf{H}_i, \quad i=1, 2, 3, 4, \tag{4}$$

in which the effective fields are

$$\begin{aligned}\mathbf{H}_1&=-\lambda\mathbf{M}_3+\Lambda\mathbf{M}_2-\mathbf{m}\times\mathbf{M}_2+\mathbf{H}_{A1}+\mathbf{H}_0,\\ \mathbf{H}_2&=-\lambda\mathbf{M}_4+\Lambda\mathbf{M}_1+\mathbf{m}\times\mathbf{M}_1+\mathbf{H}_{A2}+\mathbf{H}_0,\\ \mathbf{H}_3&=-\lambda\mathbf{M}_1+\Lambda\mathbf{M}_4-\mathbf{m}\times\mathbf{M}_4+\mathbf{H}_{A3}+\mathbf{H}_0,\\ \mathbf{H}_4&=-\lambda\mathbf{M}_2+\Lambda\mathbf{M}_3+\mathbf{m}\times\mathbf{M}_3+\mathbf{H}_{A4}+\mathbf{H}_0.\end{aligned} \tag{5}$$

The constants λ and Λ are the magnitudes of the antiferromagnetic and ferromagnetic Weiss molecular field parameters, respectively; **m** is a constant vector in the crystal *b* direction representing the Moriya interaction as a classical field; $\mathbf{H}_0$ is the static applied field; and $\gamma_0=ge/2mc$. We will employ an isotropic *g* equal to 2 throughout and so will have to replace experimental or actual values of the applied field **H** by theoretical values **H′** such that

$$H_x'=(g_a/2)H_x, \quad H_y'=(g_b/2)H_y, \quad H_z'=(g_c/2)H_z. \tag{6}$$

The anisotropy fields $\mathbf{H}_{Ai}$ represent the orthorhombic anisotropy, exclusive of the Moriya interaction, arising from magnetic dipole and pseudodipole interactions and the effect of the crystalline field. Moriya and Yosida[11] have shown that this anisotropy energy can be approximately expressed in the form

$$E_A=N^{-1}(K_1\beta^2+K_2\gamma^2) \tag{7}$$

per copper ion at the absolute zero of temperature, where N is the number of Cu^{2+} ions per unit volume and β and γ are the direction cosines of the sublattice magnetization vector relative to the *b* and *c* axes, respectively. (The crystal coordinates *abc* are equivalent to the Cartesian coordinates *xyz* in the same order.) Since the anisotropy fields seen by each sublattice must be equivalent, the expressions for these fields are

$$\mathbf{H}_{Ai}=-\tfrac{1}{2}M_0^{-2}(0,K_1M_i^y,K_2M_i^z), \tag{8}$$

where M_0 is the magnitude of the sublattice magnetization vector at 0°K.

To find the equilibrium position and natural frequencies, we transform Eqs. (4) and (5) to four independent coordinate systems $X_iY_iZ_i$ such that Z_i is in the equilibrium direction of $\mathbf{M}_i$. These unitary transformations are

$$\begin{aligned}x_i&=X_i\cos\phi_i-Y_i\sin\phi_i\sin\psi_i+Z_i\sin\phi_i\cos\psi_i,\\ y_i&=Y_i\cos\psi_i+Z_i\sin\psi_i,\\ z_i&=-X_i\sin\phi_i-Y_i\cos\phi_i\sin\psi_i+Z_i\cos\phi_i\cos\psi_i,\end{aligned} \tag{9}$$

where the ϕ_i are the angles of rotation about the *y* axis in a positive sense and the ψ_i are the angles of rotation about the new X_i axes in a negative sense. [A rotation in the positive (negative) sense is defined as one which would cause a right-handed screw to advance (retreat) along the axis of rotation.] Following these transformations it is convenient to make the substitutions

$$\begin{aligned}\phi_1&=\tfrac{1}{2}\pi-\theta_1, & \phi_2&=\tfrac{1}{2}\pi+\theta_2,\\ \phi_3&=\tfrac{3}{2}\pi-\theta_3, & \phi_4&=\tfrac{3}{2}\pi+\theta_4.\end{aligned} \tag{10}$$

The angles θ_i and ψ_i are shown in Fig. 3. Terms like M^XM^Y in the equations of motion can be dropped since

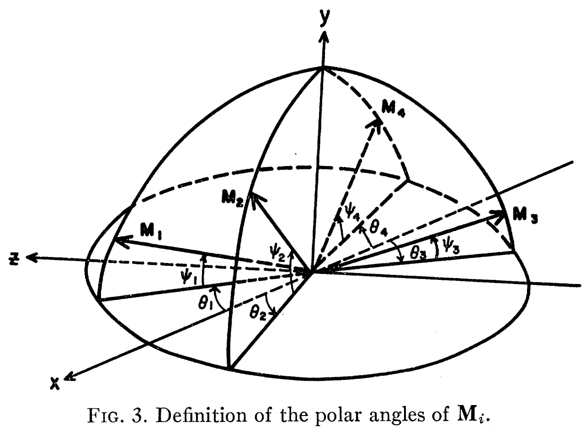

FIG. 3. Definition of the polar angles of $\mathbf{M}_i$.

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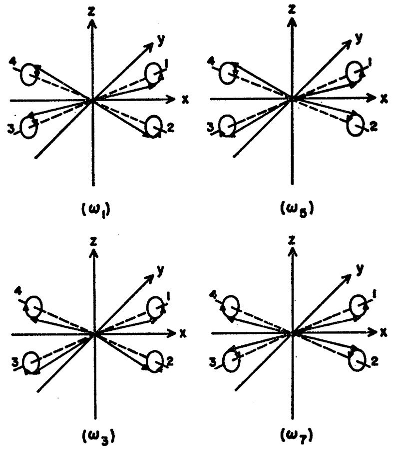

FIG. 4. Normal modes of canted $CuCl_2 \cdot 2H_2O$.

the magnetization vectors are assumed to be predominantly in the Z directions. Let all $M_i^Z = M_0$ and define $H_\lambda = \lambda M_0$, $H_\Lambda = \Lambda M_0$, $H_m = mM_0$, $H_b = \frac{1}{2}(K_1/M_0)$, and $H_c = \frac{1}{2}(K_2/M_0)$. Assume all M^X and M^Y proportional to $\exp(i\omega t)$.[12]

In the absence of an applied field in the y direction all $\psi_i = 0$ and the equilibrium position is in the $xz(ac)$ plane. When the applied field in the xz plane is also zero, then all $\theta_i = \theta$ and the equilibrium condition on θ is

$$\tan 2\theta = 2H_m/(2H_\Lambda + H_c). \tag{11}$$

Since $H_\Lambda \gg H_m \gg H_c$, we can write

$$\theta \approx \theta_0 \equiv H_m/2H_\Lambda, \tag{12}$$

which is correct through terms of order θ_0^2.

The secular determinant is formed from the remaining eight linear, independent equations in M_i^X and M_i^Y:

$$\begin{array}{cccccccc} M_1^X & M_2^X & M_3^X & M_4^X & M_1^Y & M_2^Y & M_3^Y & M_4^Y \\ \end{array}$$
$$\begin{vmatrix} \epsilon & 0 & 0 & 0 & p & -H_\Lambda & H_\lambda & 0 \\ 0 & \epsilon & 0 & 0 & -H_\Lambda & p & 0 & H_\lambda \\ 0 & 0 & \epsilon & 0 & H_\lambda & 0 & p & -H_\Lambda \\ 0 & 0 & 0 & \epsilon & 0 & H_\lambda & -H_\Lambda & p \\ -q & r & H_\lambda & 0 & \epsilon & 0 & 0 & 0 \\ r & -q & 0 & H_\lambda & 0 & \epsilon & 0 & 0 \\ H_\lambda & 0 & -q & r & 0 & 0 & \epsilon & 0 \\ 0 & H_\lambda & r & -q & 0 & 0 & 0 & \epsilon \end{vmatrix}, \tag{13}$$

where $\epsilon = -i\omega/\gamma_0$, $p = (H_\lambda + H_\Lambda + H_m\theta_0 + H_b)$, $q = [H_\lambda + H_\Lambda(1-2\theta_0^2) + 2H_m\theta_0 + H_c]$, and $r = [H_\Lambda(1-2\theta_0^2) + 2H_m\theta_0]$ Setting the determinant equal to zero we find the eight resonance frequencies:

$$\begin{aligned} \omega_1 &= -\omega_2 = \gamma_0(2H_\lambda H_c)^{\frac{1}{2}}, \\ \omega_3 &= -\omega_4 = \gamma_0(2H_\lambda H_b')^{\frac{1}{2}}, \\ \omega_5 &= -\omega_6 = \omega_7 = -\omega_8 = 2\gamma_0[H_\Lambda(H_\lambda + H_\Lambda)]^{\frac{1}{2}}, \end{aligned} \tag{14}$$

where $H_b' = H_b + H_m^2/2H_\Lambda$.

The diagonalizing matrix for (13), i.e., the matrix in which the columns are the eigenvectors of the resonance matrix and represent the normal modes corresponding to the resonance frequencies (eigenvalues), is proportional to

$$\begin{array}{c|cccccccc|} & \omega_1 & \omega_2 & \omega_3 & \omega_4 & \omega_5 & \omega_6 & \omega_7 & \omega_8 \\ M_1^X & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ M_2^X & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\ M_3^X & 1 & 1 & -1 & -1 & -1 & -1 & 1 & 1 \\ M_4^X & 1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 \\ M_1^Y & i\mu & -i\mu & i\nu & -i\nu & i\sigma & -i\sigma & i\tau & -i\tau \\ M_2^Y & i\mu & -i\mu & i\nu & -i\nu & -i\sigma & i\sigma & -i\tau & i\tau \\ M_3^Y & i\mu & -i\mu & -i\nu & i\nu & -i\sigma & i\sigma & i\tau & -i\tau \\ M_4^Y & i\mu & -i\mu & -i\nu & i\nu & i\sigma & -i\sigma & -i\tau & i\tau \end{array}, \tag{15}$$

where $\mu = (H_c/2H_\lambda)^{\frac{1}{2}}$, $\nu = (2H_\lambda/H_b')^{\frac{1}{2}}$, $\sigma = [(H_\lambda + H_\Lambda)/H_\Lambda]^{\frac{1}{2}}$, and $\tau = \sigma^{-1}$. In a given mode all four sublattice magnetization vectors precess in equal size ellipses about their individual equilibrium directions. The normal modes are shown in Fig. 4.

Modes 1 and 2 represent a net magnetization vector oscillating in the crystal b direction. The corresponding frequency, $|\omega| = \gamma_0(2H_\lambda H_c)^{\frac{1}{2}}$, is one of the antiferromagnetic resonance frequencies derived by Yosida[3] and others[4–6] for a two sublattice model. Modes 3 and 4, which also correspond to antiferromagnetic resonance, have a net magnetization vector oscillating along the c axis. In this case the four-sublattice model resonance frequency differs from that of the two-sublattice model by the inclusion of a term proportional to the Moriya coupling constant, but reduces to the latter in the absence of the Moriya interaction.

The net magnetization vector oscillates along the a axis in modes 5 and 6 and is zero in modes 7 and 8. These modes correspond to the relatively high frequencies $|\omega| = 2\gamma_0[H_\Lambda(H_\lambda + H_\Lambda)]^{\frac{1}{2}}$ which we have termed exchange frequencies since they are proportional to both the ferromagnetic and antiferromagnetic exchange fields and are approximately an order of magnitude greater than the antiferromagnetic resonance frequencies. Although the Moriya interaction constant does not appear explicitly in the exchange frequencies, the corresponding modes are dependent on the canting between ferromagnetic sublattices. In the absence of the Moriya interaction this canting vanishes and the four sublattices degenerate to two. In this case the exchange modes do not appear. In view of this fact, an experimental attempt to excite mode 5 (or 6) with an rf field should confirm or deny the existence of the Moriya interaction in $CuCl_2 \cdot 2H_2O$, and in the case of confirmation should provide quantitative information on the strength of the exchange interactions. The frequencies ω_5 and ω_7 are not actually degenerate, but differ by terms of order θ_0^2. However, since only mode 5 is excitable by an rf field, the difference between ω_5 and ω_7 is not significant at present.

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[12] Although M^X and M^Y are actually proportional to $\sin\omega t$ or $\cos\omega t$, the phase relations can be identified from the complex amplitudes of the normal modes.

IV. CLASSICAL CALCULATION AT 0°K; EFFECT OF A FIELD

We now consider the effect of a static magnetic field applied parallel to each of the crystal axes. To have a detectable effect on the magnitude of the exchange frequencies the applied field will have to be quite large, of the order of magnitude of the exchange fields. Only for materials such as $CuCl_2 \cdot 2H_2O$ and $MnCl_2 \cdot 4H_2O$ with very low Néel temperatures are large enough fields currently obtainable. We will see that only in the b direction in copper chloride can a field be applied that is large enough to affect noticeably the exchange frequencies without simultaneously overcoming the Moriya interaction on which they are dependent.

Twenty-five years ago Néel[13] predicted the existence of a critical field strength in antiferromagnetics for the case of a field applied along the axis of easy magnetization. At this critical value of the field the antiparallel magnetizations would turn from the easy axis to a hard(er) axis perpendicular to it. This spin flopping was observed in $CuCl_2 \cdot 2H_2O$ at a field strength of about 6500 oe by van den Handel, Gijsman, and Poulis.[14] When the spins in copper chloride swing from the a axis to the b axis (second-preferred direction) upon application of an $H_0 \approx 6500$ oe in the a direction, the canting caused by the b component of the Moriya interaction vector is reduced in proportion to the reduction in the a component of $\mathbf{S}$. Since S_a in the flopped position depends primarily on a balance of torque between the applied field and the antiferromagnetic exchange field, the reduction in S_a amounts to more than a factor of 10. At this point it should be recalled that in restricting ourselves to a four-sublattice model, we forced the net effect of the a component of the Moriya vector to be zero. Thus there is no new source of canting becoming operative after the spins have flopped to the second-preferred direction. Essentially then the situation is amenable to analysis on a two-sublattice model in which the exchange modes are nonexistent. The net result of these observations is that we can limit our consideration to $H_0 < 7000$ oe or about $(1/20)H_\lambda$ when H_0 is applied in the a direction.

A. Field in the Preferred Direction (a axis)

A small field in the a direction establishes a new equilibrium position in the xz plane. The angles shown in Fig. 3 take the values

$$\begin{aligned} \theta_1 = \theta_2 = \theta_0 - \theta_x, \\ \theta_3 = \theta_4 = \theta_0 + \theta_x, \end{aligned} \tag{16}$$

where θ_0 is still given by Eq. (12) and where $\theta_x = \theta_0[H_0/2(H_\lambda + H_\Lambda)]$. By including H_0 in the equations of motion we have a new secular determinant which has the roots

$$\begin{aligned} (\omega/\gamma_0)^2 = H_0^2 + H_\lambda[H_c(1 \pm \xi_1) + H_b'(1 \mp \xi_1)], \\ (\omega/\gamma_0)^2 = 4H_\Lambda(H_\lambda + H_\Lambda)(1 \pm \xi_2), \end{aligned} \tag{17}$$

in which the upper signs correspond to $\omega_{1,2}$ and $\omega_{5,6}$ and the lower signs to $\omega_{3,4}$ and $\omega_{7,8}$, and where $\xi_1 = [1 + 4H_0^2(H_b' + H_c)/H_\lambda(H_b' - H_c)^2]^{\frac{1}{2}}$ and $\xi_2 = H_0/[H_\Lambda(H_\lambda + H_\Lambda)]^{\frac{1}{2}}$. For $H_0 \approx 6500$ oe the maximum effect on the exchange frequencies of (17) is about ±5%. Due to the uncertainty in the magnitudes of the exchange and anisotropy fields, this range is not large enough to make an experiment feasible. The Eqs. (17) reduce to Eqs. (14) when H_0 is decreased to zero The normal modes corresponding to the frequencies (17) are given by Eqs. (15) with modified values of μ, ν, σ, and τ which are not important here.

B. Field in the z Direction (c axis)

The equilibrium positions of the four-sublattice magnetization vectors remain in the xz plane when H_0 is in the z direction For H_0 small compared with H_λ, i e , $H_0 \lesssim 10^4$ oe, the equilibrium angles are

$$\begin{aligned} \theta_1 = \theta_4 = \theta_0 + \theta_z, \\ \theta_2 = \theta_3 = \theta_0 - \theta_z, \end{aligned} \tag{18}$$

where $\theta_z = (H_0/2H_\lambda)$. The effect of this applied field amounts to only a perturbation of order θ_z^2 on the zero field resonance frequencies ω_{3-8}, but

$$\omega_1 = -\omega_2 \rightarrow \gamma_0(2H_\lambda H_c + H_0^2)^{\frac{1}{2}}, \tag{19}$$

in place of the expression (14). The normal modes (15) apply with the replacement

$$\mu \rightarrow (H_0^2 + 2H_\lambda H_c)^{\frac{1}{2}}/2H_\lambda \tag{20}$$

The action of the z field is similar to that of the Moriya field. Whereas the latter reduced the energy by canting the ferromagnetic sublattices an angle $2\theta_0$, the former has caused the antiferromagnetic sublattices to cant by an angle $2\theta_z$. Equations (18) indicate that the ferromagnetic canting does not change for $H_0 \lesssim 10^4$ oe However, when the applied field is the same order of magnitude as the antiferromagnetic exchange field, the antiferromagnetic canting is greatly increased while the ferromagnetic canting is reduced. It is convenient to describe the large-field equilibrium position by the angles

$$\begin{aligned} \theta_1 = \theta_4 = \theta, \\ \theta_2 = \theta_3 = -\theta + 2\delta, \end{aligned} \tag{21}$$

where $\delta = H_m/(2H_\Lambda + H_0 \sin\theta)$ being half the angle between sublattice magnetization vectors $\mathbf{M}_1$ and $\mathbf{M}_2$ ($\mathbf{M}_3$ and $\mathbf{M}_4$), and $\sin\theta \approx H_0/2H_\lambda$. For $H_0 \approx H_\lambda$, we have $\theta \approx 30°$ and $\delta \approx \frac{1}{2}\theta_0$.

The secular equation including a large applied field in

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[14] J. van den Handel, H. M. Gijsman, and N. J. Poulis, Physica **18**, 862 (1952).

the z direction has the roots

$$
\begin{aligned}
\omega_1&=-\omega_2=\gamma_0(H_0^2+2H_\lambda H_c)^{\frac{1}{2}},\\
\omega_3&=-\omega_4=\gamma_0\{2H_\lambda[H_b\zeta_1+(H_m^2/2H_\Lambda)\zeta_2]\}^{\frac{1}{2}},\\
\omega_5&=-\omega_6=2\gamma_0[H_\Lambda(H_\lambda+H_\Lambda)]^{\frac{1}{2}}\\
&\qquad\qquad\times[1-H_0^2/4H_\lambda(H_\lambda+H_\Lambda)]^{\frac{1}{2}},\\
\omega_7&=-\omega_8=2\gamma_0[H_\Lambda(H_\lambda+H_\Lambda)]^{\frac{1}{2}}\\
&\qquad\qquad\times[1-(H_0H_m/2H_\Lambda^2)\zeta_3]^{\frac{1}{2}},
\end{aligned}
\tag{22}
$$

where $\zeta_1=[1+H_0^2(H_\lambda-H_\Lambda)/4H_\lambda^2H_\Lambda-H_0^4/16H_\lambda^3H_\Lambda]$, $\zeta_2=[1-H_0^2H_\Lambda/4H_\lambda^2(H_\lambda+H_\Lambda)-H_0^4/16H_\lambda^3(H_\lambda+H_\Lambda)]$, and $\zeta_3=(1-H_0^2/4H_\lambda^2)^{\frac{1}{2}}(1+H_0^2/4H_\lambda H_\Lambda)^{-1}$ If $H_0=10^5$ oe, then ω_5 in (22) is about 10% lower than the zero field ω_5, and ω_7 in (22) is about 3% lower than its zero field value. Further increase in the strength of the applied field will overcome the Moriya canting and eliminate the exchange modes altogether, so the static field dependence of ω_{5-8} does not provide a suitable tuning range for a resonance absorption experiment. The normal modes corresponding to (22) are again given by Eqs. (15) if we make the replacements

$$
\begin{aligned}
\mu&\longrightarrow(H_0^2+2H_\lambda H_c)^{\frac{1}{2}}/2H_\lambda,\\
\nu&\longrightarrow\{2H_\lambda/[H_b\zeta_1+(H_m^2/2H_\Lambda)\zeta_2]\}^{\frac{1}{2}}(1-H_0^2/2H_\lambda^2),\\
\sigma&\longrightarrow[(H_\lambda+H_\Lambda)/H_\Lambda]^{\frac{1}{2}}[1-H_0^2/4H_\lambda(H_\lambda+H_\Lambda)]^{\frac{1}{2}},\\
\tau&\longrightarrow[H_\Lambda/(H_\lambda+H_\Lambda)]^{\frac{1}{2}}[1-(H_0H_m/2H_\Lambda^2)\zeta_3]^{\frac{1}{2}}.
\end{aligned}
\tag{23}
$$

C. Field in the *y* Direction (*b* axis)

When H_0 is applied in the y direction a new equilibrium position is established in which the magnetization vectors are rotated out of the xz plane by the angles ψ_i shown in Fig. 3. In this case all $\psi_i=\psi$, where

$$\sin\psi=H_0/2H_\lambda \tag{24}$$

and all $\theta_i=\theta_0$. As in the previous situation when H_0 was in the z direction, the applied field produces a canting of the antiferromagnetic sublattices and decreases the angle between the ferromagnetic sublattices. This latter effect does not appear explicitly as it did in the z-field case because $2\theta_0$ is no longer the angle between ferromagnetic sublattices, but is now only the angle between their projections on the xz plane and as such remains constant independent of ψ.

When H_0 is small compared with the antiferromagnetic exchange field it is essentially a perturbation and appears in terms of order ψ^2. Except for the substitutions

$$
\begin{aligned}
\omega_3&\longrightarrow\gamma_0(2H_\lambda H_b'+H_0^2)^{\frac{1}{2}},\\
\nu&\longrightarrow2H_\lambda/(2H_\lambda H_b'+H_0^2)^{\frac{1}{2}},
\end{aligned}
\tag{25}
$$

the resonance frequencies and normal modes are the same as for the zero field case. The transformations (9) with $\psi\neq0$ remove the degeneracy of the Y_i axes of the four equilibrium coordinate systems with the result that the normal modes 7 and 8 now have a nonzero net magnetization vector with a component proportional to $\sin\psi$ oscillating in the z direction.

If the applied field is large, e.g., $H_0\approx H_\lambda\approx10^5$ oe, the eigenvalues of the secular equation are

$$
\begin{aligned}
\omega_1&=-\omega_2=\gamma_0[2H_\lambda H_c(1-H_0^2/4H_\lambda^2)]^{\frac{1}{2}},\\
\omega_3&=-\omega_4=\gamma_0[H_0^2+2H_\lambda H_b']^{\frac{1}{2}},\\
\omega_5&=-\omega_6=2\gamma_0[(H_\Lambda+H_0^2/4H_\lambda)(H_\lambda+H_\Lambda)]^{\frac{1}{2}},\\
\omega_7&=-\omega_8=2\gamma_0[H_\Lambda(H_\lambda+H_\Lambda-H_0^2/4H_\lambda)]^{\frac{1}{2}}.
\end{aligned}
\tag{26}
$$

For $H_0=2\times10^5$ oe, ω_5 is about twice as large as its zero-field value and ω_7 is about one-third smaller than the zero field ω_7. The eigenvectors of the normal modes are represented by Eqs. (15) after making the following substitutions:

$$
\begin{aligned}
\mu&\longrightarrow[H_c/2H_\lambda(1-H_0^2/4H_\lambda^2)]^{\frac{1}{2}},\\
\nu&\longrightarrow2H_\lambda/(H_0^2+2H_\lambda H_b')^{\frac{1}{2}},\\
\sigma&\longrightarrow[(H_\lambda+H_\Lambda)/(H_\Lambda+H_0^2/4H_\lambda)]^{\frac{1}{2}},\\
\tau&\longrightarrow[H_\Lambda/(H_\lambda+H_\Lambda-H_0^2/4H_\lambda)]^{\frac{1}{2}}.
\end{aligned}
\tag{27}
$$

The exchange resonance best suited for experimental detection is $\omega_{5,6}$. With the applied field in the y direction and a variation in its magnitude from 0 to 2×10^5 oe, the resonance frequency is increased by a factor of two. The net magnetization vector in modes 5, 6 has a component independent of H_0 oscillating in the x direction and a component proportional to H_0 oscillating in the z direction. The x and z components are 90° out of phase and are approximately equal in magnitude when $H_0\approx10^5$ oe.

V. COMPARISON WITH PREVIOUS WORK AND NUMERICAL ESTIMATES

Several authors[3–6] have derived the antiferromagnetic resonance frequencies of copper chloride dihydrate based on a two sublattice model with nearest neighbor interactions only. A detailed summary of these calculations is contained in the review article on antiferromagnetism by Nagamiya, Yosida, and Kubo[15] (NYK). Since a two-sublattice model of $CuCl_2\cdot2H_2O$ does not allow a Moriya interaction, these authors did not obtain the exchange resonance frequencies. The antiferromagnetic resonance frequencies derived in the present paper and in those reviewed by NYK are equivalent if, in the latter, the quantity K_1, representing the b component of the anisotropy, is replaced by

$$K_1'=K_1+(H_m^2/H_\Lambda)M_0, \tag{28}$$

where $K_1=2M_0H_b$. The Moriya interaction, which is an anisotropic superexchange interaction, contributes only to K_1', which otherwise arises primarily from the spin-symmetric anisotropic superexchange, and not to K_2, the c component, which is mainly due to magnetic dipole interactions.[11,15]

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[15] T. Nagamiya, K. Yosida, and R. Kubo, Suppl. Phil. Mag. **4**, 1 (1955).

The critical field strength in the a direction at which the spins turn from the a axis to the b axis is

$$H_{\mathrm{cr}}=(2H_{\lambda}H_{b}')^{\frac{1}{2}}, \tag{29}$$

which is a solution of the second of Eqs. (17) for $\omega_3=0$ and is the same expression as given by NYK when K_1 is modified as explained above. The critical field has been deduced by Ubbink[5] from antiferromagnetic resonance measurements of Ubbink *et al.*[16] as 6560 oe. Taking into account the anisotropy of the g factor, this field strength must be multiplied by $(g_a/2)=1.10$.[14,17] For the four-sublattice model the Weiss molecular field parameter λ is equal to $(2/\chi_{\perp})$. The perpendicular susceptibility has been measured[14] as 1.70×10^{-4} per gram, but must be modified for use in the present theory:

$$\chi_{\perp}(\text{theory})=(2/g_a)^2\rho\chi_{\perp}(\text{experiment}), \tag{30}$$

where $\rho=2.38$ g/cm^3. The value of the saturation sublattice magnetization is $\frac{1}{4}N\mu_B$, so we have $H_{\lambda}=1.16\times10^5$ oe. Substituting the values of H_{cr} and H_{λ} in Eq. (29) we find $H_b'=224$ oe.

Using 3-cm waves Ubblink *et al.*[16] observed antiferromagnetic resonance in $\mathrm{CuCl_2\cdot 2H_2O}$ at 1.2–1.4°K with $H_x=5050$ oe. Since there was very little temperature dependence of the resonance field below 3°K, this field strength should be approximately correct for 0°K. With $\omega/\gamma_0=3.36\times10^3$ oe corresponding to 3-cm waves, the second of Eqs. (17) was used to determine the ratio $H_c/H_b'=3.52$ and consequently $H_c=788$ oe. The experimental anisotropy fields H_b' and H_c are equivalent to $(K_1'/N)=5.22\times10^{-3}$ cm^{-1} per ion and $(K_2/N)=18.4\times10^{-3}$ cm^{-1} per ion. Moriya and Yosida,[11] with later revisions by NYK, calculated the anisotropy constants theoretically as $(K_1/N)=5.43\times10^{-3}$ cm^{-1} per ion and $(K_2/N)=34.7\times10^{-3}$ cm^{-1} per ion. If we assume $K_1'\approx2K_1$, then the theoretical anisotropy constants both exceed the experimental values by about a factor of two.

Oguchi[9] and Marshall[10] have calculated that $J'/J=0.3$ and 0.138, respectively, where J' is the ferromagnetic exchange integral and J is the antiferromagnetic exchange integral. From molecular field theory $H_{\Lambda}/H_{\lambda}=J'z'/Jz$ where $z=2$ and $z'=4$ are the numbers of nearest and next-nearest neighbors in $\mathrm{CuCl_2\cdot 2H_2O}$, respectively. Therefore we assume that $3.21\times10^4\text{ oe}\leq H_{\Lambda}\leq6.98\times10^4$ oe. Table I contains the resonance wavelength in millimeters for each normal mode for several values of the applied magnetic field. These wavelengths are predicted on the basis of the preceeding rough analysis of parameters and of course the measurement of the parameters will redetermine the values.

TABLE I. Resonance wavelengths (mm).

	Applied field in oersteds (y direction)			
Mode	0	5×10^4	10^5	2×10^5
1, 2[a]	7.90	8.10	8.83	17.4
3, 4[a]	14.9	2.04	1.03	0.514
5, 6[b]	0.774	0.712	0.583	0.390
7, 8[b]	0.774	0.791	0.842	1.27
5, 6[c]	0.469	0.450	0.407	0.301
7, 8[c]	0.469	0.478	0.500	0.667

[a] Based on experimental data.
[b] Based on Marshall's value of $J'/J=0.138$.
[c] Based on Oguchi's value of $J'/J=0.3$.

The parallel susceptibility provides a molecular field theory relation between the Moriya and exchange field parameters at 0°K,

$$\chi_{\parallel}=m^2/2\Lambda^2(\lambda+\Lambda), \tag{31}$$

but, lacking both a theory of the temperature dependence of $\chi_{\parallel}$ for a four-sublattice model and a measurement of $\chi_{\parallel}$ at a sufficiently low temperature, Eq. (31) can be used only to put an upper limit on the magnitude of H_m. Van den Handel, Gijsman, and Poulis[14] have found $\chi_{\parallel}$ to be an increasing function of temperature, their lowest determination being at 1.5°K: $\chi_{\parallel}\approx0.18\times10^{-4}$ per gram. With this value of $\chi_{\parallel}$ as an upper limit, we find $H_m\leqslant5400$ oe using Marshall's value of J'/J and $H_m\leqslant1.3\times10^4$ oe using Oguchi's value of J'/J.

Another estimate of the magnitude of the Moriya energy was obtained by comparing the theoretical expression for $\frac{1}{2}(g_b-2)$ obtained by first-order perturbation theory with the expression Moriya[7] obtained in a similar manner for the b component of the Moryia vector. The result, involving several quantitative approximations, is $D_b\approx(g_b-2)J'$. The value of g_b determined from the susceptibility measurements of van den Handel *et al.*[14] above the Néel temperature is 2.03, while that determined from the paramagnetic resonance experiments of Itoh, *et al.*[17] at room temperature is 2.075. Using the average value of g_b we find $\theta_0\approx1.6°$, and $H_m\approx2800$ oe for an average value of $H_{\Lambda}=5.1\times10^4$ oe. Finally we estimate the component of the orthorhombic anisotropy field in the b direction as $H_b=H_b'-H_m^2/2H_{\Lambda}\approx167$ oe.

VI. SPIN WAVE SPECTRA

The spin Hamiltonian for $\mathrm{CuCl_2\cdot 2H_2O}$ may be approximated as follows:

$$\begin{aligned}\mathcal{H}=2J\sum_{\langle l,m\rangle1}(\mathbf{S}_l\cdot\mathbf{S}_m)-2J'\sum_{\langle l,m\rangle2}(\mathbf{S}_l\cdot\mathbf{S}_m)\\ -2\mathbf{D}\cdot\sum_{\langle l,m\rangle2}(\mathbf{S}_l\times\mathbf{S}_m)\\ +N^{-1}S^{-2}\sum_{l}[K_1'(S_l^y)^2+K_2(S_l^z)^2],\end{aligned} \tag{32}$$

where $\langle\ \rangle1$ under the summation sign means pairs of nearest-neighbor cations; $\langle\ \rangle2$ means pairs of next-nearest-neighbor cations; and J, J', and $\mathbf{D}$ are positive constants representing the antiferromagnetic, ferromag-

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[16] J. Ubbink, J. A. Poulis, H. J. Gerritsen, and C. J. Gorter, Physica **18**, 361 (1952).

[17] J. Itoh, M. Fujimoto, and H. Ibamoto, Phys. Rev. **83**, 852 (1951).

netic, and Moriya exchange integrals, respectively. Although the anisotropy terms in this Hamiltonian have the form of single-spin anisotropy, which is constant for $S=\frac{1}{2}$, these terms are actually the phenomenological resultant form of the two-spin magnetic dipole and pseudo-dipole interactions derived for $CuCl_2 \cdot 2H_2O$ by Moriya and Yosida.[11] The resemblance to single-spin anisotropy is due to the symmetry of the sublattice magnetization vectors with respect to the crystal axes. Since the anisotropy in (32) depends not on the magnitude of the individual spin quantum number, but only on the angles between the macroscopic magnetization vectors and the crystal axes, we will assume for our spin wave treatment that this single-spin form of the anisotropy behaves as if $S>\frac{1}{2}$. The constants K_1' and K_2 have the same values as in the classical calculation.

Adapting the Holstein-Primakoff[18] method of spin deviation operators to our four-sublattice model, introducing spin waves, and making appropriate canonical transformations, we reduce the Hamiltonian (32) to the harmonic oscillator approximation. Aside from the zero point energy we find the following spin wave spectra for small **k**:

$$\begin{aligned} E_{1,2}(k) &= [8JzK_2/N+2(Jz)^2(d+\alpha d')k^2]^{\frac{1}{2}}, \\ E_{3,4}(k) &= [2Jz(4K_1'/N+D^2z'/2J') \\ &\qquad +2(Jz)^2(d+\alpha d')k^2]^{\frac{1}{2}}, \qquad (33) \\ E_{5,6}(k) &= E_{7,8}(k) = 2\{J'z'(Jz+J'z') \\ &\qquad +2(Jz)^2[d-(\alpha+2\alpha^2)d']k^2\}^{\frac{1}{2}}, \end{aligned}$$

where d and d' are nearest- and next-nearest-neighbor structure factors, $\alpha=J'z'/Jz$, and we have now inserted $S=\frac{1}{2}$ as the magnitude of the spin quantum number for a single atom. The equilibrium position is in the xz plane and at 0°K is given by $\theta_0=D/2J'$ which is equivalent to the value of the equilibrium angle derived classically. The classical frequencies (14) are equivalent to the energy eigenvalues (32) at $T=0$°K for $\mathbf{k}=0$.

The spin wave spectra may be considered to have low- and high-frequency branches which are somewhat analogous to acoustical and optical branches in that the magnetization vectors of next-nearest-neighbor sublattices 1 and 2 (3 and 4) oscillate in phase in the low-frequency modes and 180° out of phase in the high-frequency modes. The introduction of the Moriya energy has not altered the minimum energy needed to excite a $\mathbf{k}=0$ spin wave. This energy is $E_{3,4}(0)$ and corresponds to about a 1°K gap. As pointed out by Eisele and Keffer,[2] the existence of such a gap leads to a complicated temperature dependence for the magnetic specific heat compared to the T^3 dependence of an isotropic antiferromagnet. Petersen and Phillips,[19] however, have observed a T^3 dependence of the magnetic specific heat of $CuCl_2 \cdot 2H_2O$ below 0.55°K contrary to theoretical prediction. This discrepancy may be explained by the theory of Pincus and Winter[20] in which the magnetostrictive terms in the Hamiltonian produce a magnon component in the thermal phonon spectrum allowing phonons to participate directly in magnetic processes.

VII. CONCLUSION

The introduction of the Moriya energy into the spin Hamiltonian for copper chloride dihydrate has resulted in a set of high frequency exchange resonance modes not previously predicted or observed. Although the exchange frequencies do not involve the Moriya constant explicitly, the amplitude of the exchange normal modes is proportional to the canting between next-nearest-neighbor spins which is caused by the Moriya interaction. We propose a resonance absorption experiment on $CuCl_2 \cdot 2H_2O$ in the antiferromagnetic state below 4.3°K to detect the exchange resonances and verify the existence of the Moriya interaction. The rf field should be in the crystal a or c direction with a wavelength of approximately 0.6 mm and the static applied field should be in the crystal b direction with a magnitude varied from about 5×10^4 to 2×10^5 oe.

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[18] T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

[19] R. G. Petersen and N. E. Phillips, J. Chem. Phys. **34**, 1463 (1961).

[20] P. Pincus and J. Winter, Phys. Rev. Letters **7**, 269 (1961).