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# Low-Temperature Spin Orientation in Cobalt Tutton's Salt. II

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The spin orientation of the $Co^{+2}$ ions in $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$ calculated in a previous work was extended to include exchange in addition to the dipolar and hyperfine interactions. The exchange was found to have a small effect on the orientation of the spins, but a significant decrease occurred in the value of the minimum energy.

## I. INTRODUCTION

Cobalt Tutton's salt Co $(NH_4)_2SO_4 \cdot 6H_2O$ is widely used in attaining low temperatures by adiabatic demagnetization, and therefore there is considerable interest in its properties. Measurements have been made of its crystal structure, specific heat, transition temperature, magnetic susceptibility, $g$ factor, hyperfine coupling constant, and other properties.[1–6] As a result it is desirable to compare these measurements with calculated values. With this aim in mind we computed the ground-state spin orientation of the cobalt ions in cobalt Tutton's salt in a previous work[7] which will be referred to as I. The influence of the dipolar and hyperfine interactions were taken into account explicitly. In the present paper the calculations will be extended to include the effect of exchange.

In an earlier work Garrett[3] had pointed out that four possible interactions should influence the specific heat, namely, (i) the Stark effect, (ii) the dipolar interaction $E_{DD}$, (iii) the nuclear electronic interaction $E_N$, and (iv) exchange $E_{ex}$. Kramers's degeneracy eliminated the need to consider the Stark effect, and in I the dipolar and nuclear electronic interactions were included. Garrett[3] assumed that the relative contributions to the specific heat of the dipolar and nuclear electronic interactions have the following magnitude:

$$|E_{DD}|/|E_N| \sim 1.18, \tag{1}$$

and his reasoning leads one to expect the ratio of interactions (iv) to (iii) to be

$$|E_{ex}|/|E_N| \sim 0.5 . \tag{2}$$

Our calculations indicate that the relative contributions to the specific heat of these particular interactions are in accordance with the following ratios:

$$|E_{DD}|/|E_N| \sim 1.15 , \tag{3}$$

$$|E_{ex}|/|E_N| \sim 0.74 . \tag{4}$$

The method followed in carrying out these calculations will be described after a brief discussion of each of the three relevant interactions. Relation (4) was calculated with $f = 2.5$, as defined in Sec. V; see also Table II.

## II. DIPOLE-DIPOLE INTERACTION

Before proceeding with the new calculation it will be convenient to summarize the method adopted in I. The Luttinger-Tisza[8] approach was employed to obtain a dipolar matrix $\underline{a}$ which takes into account the anisotropies[9] of the lattice. It includes the interaction between ions of type $A$, that between ions of type $B$, and also the interactions between both types of ions. The $6 \times 6$ matrix $\underline{a}$ was diagonalized to find the six eigenvalues $E$ and their associated eigenvectors $\vec{V}$. The six eigenvectors not only form an orthonormal set, but they also satisfy the so-called strong constraint

$$\sum_{i=1}^{3} V_i^2 = \sum_{j=4}^{6} V_j^2 = 1,$$

where the $V_i$ are the three components for ions of type $A$ and the $V_j$ are the components of type $B$. The minimum energy has a value

$$E_{DD\,\mathrm{min}} = -0.0399\ \mathrm{cm}^{-1}. \qquad (5)$$

The six energies $E$ and their corresponding eigenvectors are given in I.

## III. ELECTRON NUCLEAR INTERACTION

The next step is the calculation of the effective magnetic field $H$ to be introduced into the spin Hamiltonian. In the laboratory coordinate system the matrix $\underline{a}$ was written in the form

$$\underline{a} = \tfrac{1}{4}\mu_B^2\, \underline{G}\,\underline{D}\,\underline{G}\,, \qquad (6)$$

where the $6\times 6$ matrices $\underline{G}$ and $\underline{D}$ arise from the $g$ factor and dipolar operators, respectively, and $\mu_B$ is the Bohr magneton. From this matrix $\underline{a}$ one may extract an operator $\underline{H}^D_{\mathrm{op}}$,

$$\underline{H}^D_{\mathrm{op}} = \tfrac{1}{2}\mu_B\, \underline{D}\,\underline{G}\,, \qquad (7)$$

which produces the magnetic field vector $\vec{H}$,

$$\vec{H} = \underline{H}^D_{\mathrm{op}} \cdot \vec{V}, \qquad (8)$$

whose first three components constitute the magnetic field at site $A$, and whose remaining three components give the magnetic field at the $B$ site arising from all of the other magnetic moments in the lattice. This occurs because the average spin orientation is given by the vector $\vec{V}$,

$$\vec{V} = \begin{bmatrix} \langle S^A\rangle \\ \langle S^B\rangle \end{bmatrix}, \qquad (9)$$

whose first three components arise from spin $\vec{S}^A$ and the remaining three from $\vec{S}^B$.

Since $\vec{H}$ is the local magnetic field at the spin sites $A$ and $B$ it is appropriate to introduce it into the spin Hamiltonian

$$\mathcal{H} = \mu_B \vec{H}\cdot \underline{g}\cdot \vec{S} + \vec{S}\cdot \underline{T}\cdot \vec{I}, \qquad (10)$$

which produces 16 eigenvalues and 16 associated eigenvectors for each spin type corresponding to the effective electronic spin $S=\frac{1}{2}$ and the nuclear spin $I=\frac{7}{2}$. The lowest eigenvalue corresponding to the ground state provides the eigenvector $|\phi_{\mathrm{min}}\rangle$, which may be employed to calculate the expectation value of the spin,

$$\langle S^\alpha\rangle = \langle \phi^\alpha_{\mathrm{min}} | S | \phi^\alpha_{\mathrm{min}}\rangle, \qquad (11)$$

where $\alpha$ means $A$ or $B$. These spin expectation values are then used in Eq. (9) to produce a new vector $\vec{V}$ which provides a new local magnetic field (8) for use in the Hamiltonian (10). The process of alternately calculating $\vec{H}$ and solving for $|\phi_{\mathrm{min}}\rangle$ is repeated until self-consistency is obtained. The final result provides the minimum energy values

$$E_{DD} + E_N = -0.0744\ \mathrm{cm}^{-1}. \qquad (12)$$

Combining this result with Eq. (5) gives the ratio

$$E_{DD}/E_N = 1.16$$

in agreement with (3). These results constitute the energies of the magnetic ground state at 0 °K in the absence of exchange.

In Table I we give the energy and orientation of the spins for the ground state, and also the magnetic field at each site. The coordinate systems used in the calculation are shown in Fig. 1, and the orientations of the spins are presented in Fig. 2. Column 2 of Table I lists values calculated with summations over lattice sites within a sphere of radius 100 Å, and column 3 gives the same quantities calculated with a larger sphere of radius 350 Å. These latter quantities were used for the calculations described in Sec. IV.

## IV. EXCHANGE INTERACTION

The object of the present paper is to extend the calculation outlined above by taking into account the additional interaction of exchange. In order to calculate the contribution of exchange to the minimum energy and spin orientation we make use of the theoretical calculations of Nakamura and Uryû[10] and Uryû.[11] They followed Abragam and Pryce[12] by starting with the $L=3$, $S=\frac{3}{2}$ wave function of the free $Co^{+2}$ ion. Some of the degeneracy is removed by the crystalline electric fields to produce a new effective orbital angular momentum $l'=1$. The spin-orbit coupling further raises the degeneracy to produce a lowest level which is characterized by the quantum number $m$,

TABLE I. Calculated values of the effective field $\vec{H}_{\mathrm{eff}}$, ground-state energy, and orientation $(\theta_M, \phi)$ of the spins taking into account the dipole-dipole and hyperfine interactions only, with exchange neglected. Column 2 presents values determined in the previous study (I) and column 3 lists more refined values used in the present calculations.

| | Radius of 100 Å | Radius of 350 Å |
|---|---|---|
| $H_{\mathrm{eff}}$ (G) | 140 | 178 |
| Ground-state energy ($\mathrm{cm}^{-1}$) | −0.0678 | −0.0744 |
| $\lvert\theta_M\rvert$ | 10° | 11° |
| $\phi$ | 19° | 21° |

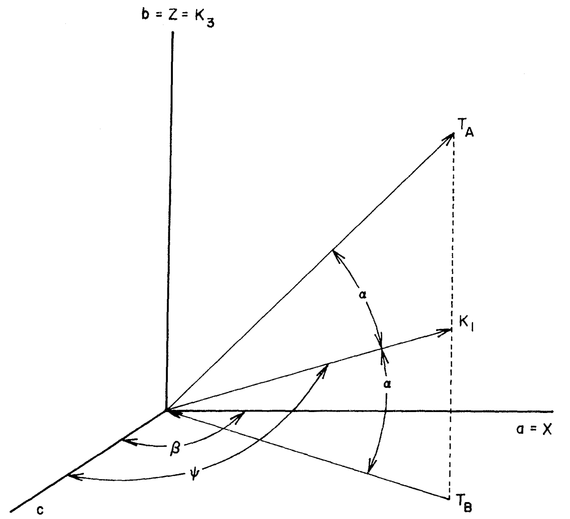


FIG. 1. Coordinate system where $k_1$ lies in the $ac$ plane, $\vec{T}_A$ is at an angle $\alpha$ above this plane, $\vec{T}_B$ is $\alpha$ below the plane, $\alpha = 34°$, $\beta = 106.56°$, and $\psi = 130°$.

$$m = m_{l'} + m_s = \pm \tfrac{1}{2} , \tag{13}$$

where $m_{l'}$ denotes the eigenvalue of the $z$ component of $l'$ and $m_s$ is the eigenvalue of the $z$ component of the spin $S$. The wave functions $\psi_m$ are linear combinations of the functions $\psi_{(m_{l'} m_s)}$ in the absence of spin-orbit coupling subject to condition (13):

$$\begin{aligned} \psi_{1/2} &= a\psi_{(-1,3/2)} + b\psi_{(0,1/2)} + c\psi_{(1,-1/2)} , \\ \psi_{-1/2} &= a\psi_{(1,-3/2)} = b\psi_{(0,-1/2)} + c\psi_{(-1,1/2)} . \end{aligned} \tag{14}$$

The calculated values of the coefficients are

$$a = -0.8959, \quad b = 0.2772 , \quad c = -0.3471 ,$$

$$a^2 + b^2 + c^2 = 1. \tag{15}$$

These wave functions will be employed to calculate exchange matrix elements.

The Hamiltonian term for exchange is given by

$$\mathcal{H}_{\mathrm{ex}} = 2 \sum_{i>j} J_{ij} \vec{S}_i \cdot \vec{S}_j \tag{16}$$

and its representation in the tetragonal system for a pair of equivalent nearest-neighbor spins $[(\mathcal{H}_{\mathrm{ex}}^{AA})_{ij}$ or $(\mathcal{H}_{\mathrm{ex}}^{BB})_{ij}]$ with $J_{ij} = J_1$ is as follows:

$$\mathcal{H}_{\mathrm{ex}} = \begin{pmatrix} -\frac{1}{2}J_1 C^2 & 0 & 0 & 0 \\ 0 & \frac{1}{2}J_1 C^2 & -4J_1 D^2 & 0 \\ 0 & -4J_1 D^2 & \frac{1}{2}J_1 C^2 & 0 \\ 0 & 0 & 0 & -\frac{1}{2}J_1 C \end{pmatrix} . \tag{17}$$

This matrix representation corresponds to an equivalent Hamiltonian with terms of the type

$$(\mathcal{H}_{\mathrm{ex}})_{ij} = J_{\perp} (S_x^i S_x^j + S_y^i S_y^j) + J_{\parallel} S_z^i S_z^j , \tag{18}$$

where

$$\begin{aligned} &J_{\perp} = -8J_1 D^2, \qquad J_{\parallel} = -2J_1 C^2, \\ &C = 1 + 2(a^2 - c^2), \qquad D = b^2 + \sqrt{3}ac . \end{aligned} \tag{19}$$

In the case of different spins $[(\mathcal{H}_{\mathrm{ex}}^{AB})_{ij} = (\mathcal{H}_{\mathrm{ex}}^{BA})_{ij}]$ the matrix is somewhat more complicated, and for a pair of close spins with $J_{ij} = J_2$ it has the explicit form

$$\mathcal{H}_{\mathrm{ex}} = \begin{pmatrix} \frac{1}{2}J_2 C^2 \cos 2\alpha & -\frac{1}{2}J_2 CD \sin 2\alpha & \frac{1}{2}J_2 CD \sin 2\alpha & 2J_2 D^2(1+\cos 2\alpha) \\ -\frac{1}{2}J_2 CD \sin 2\alpha & -\frac{1}{2}J_2 C^2 \cos 2\alpha & -2J_2 D^2(1-\cos 2\alpha) & -\frac{1}{2}J_2 CD \sin 2\alpha \\ \frac{1}{2}J_2 CD \sin 2\alpha & -2J_2 D^2(1-\cos 2\alpha) & -\frac{1}{2}J_2 C^2 \cos^2 2\alpha & \frac{1}{2}J_2 CD \sin 2\alpha \\ 2J_2 D^2(1+\cos 2\alpha) & -\frac{1}{2}J_2 CD \sin 2\alpha & \frac{1}{2}J_2 CD \sin 2\alpha & \frac{1}{2}J_2 C^2 \cos 2\alpha \end{pmatrix} . \tag{20}$$

This corresponds to the following equivalent Hamiltonian:

$$(\mathcal{H}_{\mathrm{ex}})_{ij} = J_a S_x^i S_x^j + J_b S_y^i S_y^j + J_c S_z^i S_z^j + J_d (S_z^i S_x^j - S_x^i S_z^j) , \tag{21}$$

where

$$\begin{aligned} &J_a = 8J_2 D^2 \cos 2\alpha, \qquad J_b = -8J_2 D^2, \\ &J_c = 2J_2 C^2 \cos 2\alpha, \qquad J_d = -4J_2 CD \sin 2\alpha , \end{aligned} \tag{22}$$

and $\alpha$ is the angle shown in Fig. 1. These equivalent Hamiltonians are in forms that are convenient for use in calculations.

Crystallographic structure data on Co Tutton's salt[6] indicate that an ion of type $A$ at the (0, 0, 0) position has two $A$-type nearest-neighbor ions 6.24 Å away at (0, 0, ± 1) and four $B$-type next nearest neighbors 7.85 Å distant at the positions ($\pm\frac{1}{2}$, $\pm\frac{1}{2}$, 0). Each nearest neighbor has an exchange interaction energy $I_{AA}$ and each next nearest neighbor has an exchange energy $I_{AB}$ with the ion $A$. Therefore the total exchange energy $E_A$ associated with the ion

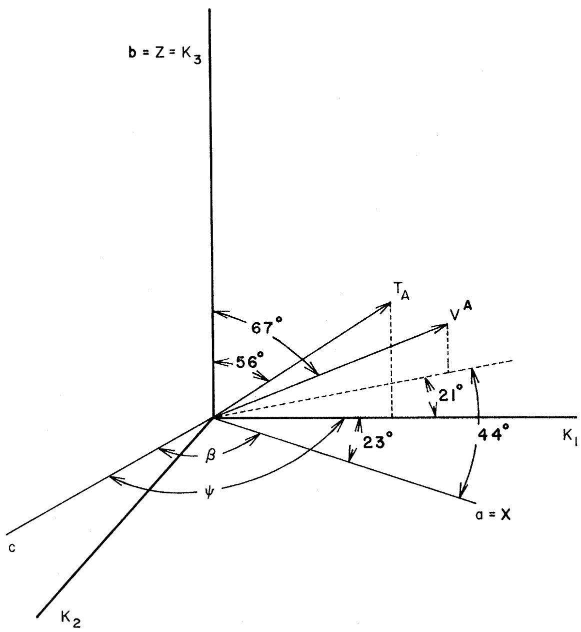


FIG. 2. Spin orientation at 0 °K including the dipole-dipole and hyperfine interactions. From the figure $\theta_M = (67° - 56°) = 11°$ and $\phi = 21°$.

in an $A$ site and the analogous energy $E_B$ associated with an ion in a $B$ site are given by

$$E_A = 2I_{AA} + 4I_{AB}, \quad E_B = 2I_{BB} + 4I_{AB}, \tag{23}$$

where, of course,

$$I_{AB} = I_{BA} .$$

## V. EFFECTIVE FIELD APPROXIMATION

The Hamiltonians (18) and (21) for the individual exchange interaction between pairs of like and unlike spins, respectively, may be summed over the appropriate neighbors in the manner of Eq. (23). Before carrying out this summation, it will be appropriate to consider each Hamiltonian [(18) and (21)] as the energy of a spin $S^i$ in the effective magnetic field arising from the exchange interaction with the other nearby spins. This procedure will be carried out first for the nearest neighbors ($AA$ and $BB$ cases) and then for the next nearest neighbors ($AB$ case).

For the $AA$ and $BB$ cases, Eq. (18) may be written as

$$\mathcal{H}^i_{\text{ex}} = \sum_{j=1}^{2} \left[ J_\perp (S^i_x S^j_x + S^i_y S^j_y) + J_\parallel S^i_z S^j_z \right] , \tag{24}$$

which may be put in the form

$$\mathcal{H}_{\text{ex}} = q_\perp \mu_B (S_x H_x + S_y H_y) + g_\parallel \mu_B S_z H_z , \tag{25}$$

where the superscript $i$ on the spin operators is omitted, and the effective field $\vec{H}^{AA}_{\text{eff}}$ has the three components

$$H_x = \sum_{j=1}^{2} \frac{J_\perp S^j_x}{g_\perp \mu_B} = \frac{2J_\perp \langle S_x \rangle}{g_\perp \mu_B} ,$$

$$H_y = \sum_{j=1}^{2} \frac{J_\perp S^j_y}{g_\perp \mu_B} = \frac{2J_\perp \langle S_y \rangle}{g_\perp \mu_B} , \tag{26}$$

$$H_z = \sum_{j=1}^{2} \frac{J_\parallel S^j_z}{g_\parallel \mu_B} = \frac{2J_\parallel \langle S_z \rangle}{g_\parallel \mu_B} .$$

In the Weiss approximation we assume that each $S$ can be replaced by its average value $\langle S \rangle$. This effective field may be derived from the operator

$$\underline{H}^{AA}_{\text{op}} = \begin{pmatrix} 2J_\perp/g_\perp \mu_B & 0 & 0 \\ 0 & 2J_\perp/g_\perp \mu_B & 0 \\ 0 & 0 & 2J_\parallel/g_\parallel \mu_B \end{pmatrix}, \tag{27}$$

and in the formalism of Eq. (7) it has the form

$$\vec{H}^{AA}_{\text{eff}} = \underline{H}^{AA}_{\text{op}} \cdot \langle \vec{S} \rangle , \tag{28}$$

where the components of $\langle \vec{S} \rangle$ are defined by Eq. (26).

For the $AB$ case the treatment is the same as for the $AA$ case, but the actual expressions are somewhat more complex. The Hamiltonian (21)

$$\mathcal{H}^i_{\text{ex}} = \sum_{j=1}^{4} \left[ J_a S^i_x S^j_x + J_b S^i_y S^j_y + J_c S^i_z S^j_z + J_d (S^i_z S^j_x - S^i_x S^j_z) \right] \tag{29}$$

may be put in the form of Eq. (25), where in this case the components of the effective field are

$$H_x = 4(J_a \langle S_x \rangle - J_d \langle S_z \rangle)/g_\perp \mu_B ,$$

$$H_y = 4J_b \langle S_y \rangle / g_\perp \mu_B , \tag{30}$$

$$H_z = 4(J_d \langle S_x \rangle + J_c \langle S_z \rangle)/g_\parallel \mu_B .$$

This effective field may be derived from the operator

$$\underline{H}^{AB}_{\text{op}} = \begin{pmatrix} 4J_a/g_\perp \mu_B & 0 & -4J_d/g_\perp \mu_B \\ 0 & 4J_b/g_\perp \mu B & 0 \\ 4J_d/g_\parallel \mu_B & 0 & 4J_c/g_\parallel \mu_B \end{pmatrix} \tag{31}$$

to give the analog of Eqs. (8) and (28),

$$\vec{H}^{AB}_{\text{eff}} = \underline{H}^{AB}_{\text{op}} \cdot \langle \vec{S} \rangle . \tag{32}$$

Combining Eqs. (27) and (31) gives the total operator

$$\underline{H}^J_{\rm op} = \begin{pmatrix} \frac{2J_\perp}{g_\perp \mu_B} & 0 & 0 & \frac{4J_a}{g_\perp \mu_B} & 0 & \frac{4J_d}{g_\perp \mu_B} \\ 0 & \frac{2J_\perp}{g_\perp \mu_B} & 0 & 0 & \frac{4J_b}{g_\perp \mu_B} & 0 \\ 0 & 0 & \frac{2J_\parallel}{g_\parallel \mu_B} & -\frac{4J_d}{g_\parallel \mu_B} & 0 & \frac{4J_c}{g_\parallel \mu_B} \\ \frac{4J_a}{g_\perp \mu_B} & 0 & -\frac{4J_d}{g_\perp \mu_B} & \frac{2J_\perp}{g_\perp \mu_B} & 0 & 0 \\ 0 & \frac{4J_b}{g_\perp \mu_B} & 0 & 0 & \frac{2J_\perp}{g_\perp \mu_B} & 0 \\ \frac{4J_d}{g_\parallel \mu_B} & 0 & \frac{4J_c}{g_\parallel \mu_B} & 0 & 0 & \frac{2J_\parallel}{g_\parallel \mu_B} \end{pmatrix} . \qquad (33)$$

Notice that the $(H^J_{\rm op})_{43}$ and $(H^J_{\rm op})_{61}$ components are different from their respective counterparts $(H^J_{\rm op})_{34}$ and $(H^J_{\rm op})_{16}$.[11]

The most general form of the bilinear spin-spin coupling between two spins $S_1$ and $S_2$ can be written as follows:

$$V_{12} = \vec{S}_1 \cdot \underline{K}_s \cdot \vec{S}_2 + \vec{S}_1 \cdot \underline{K}_a \cdot \vec{S}_2 \ , \qquad (34)$$

where $\underline{K}_s$ and $\underline{K}_a$, respectively, represent symmetrical and antisymmetrical tensors.[13]

The antisymmetrical parts acts to cant the spins, while the symmetrical part tends to make them parallel. The operator $\underline{H}^D_{\rm op}$ given in Eq. (7) has the following antisymmetrical part in the tetragonal system, in units of gauss:

$$\begin{pmatrix} 0 & 0 & -110 & 0 & 0 & 43 \\ 0 & 0 & -107 & 0 & 0 & -10 \\ 110 & 107 & 0 & 43 & -10 & 0 \\ 0 & 0 & -43 & 0 & 0 & 110 \\ 0 & 0 & 10 & 0 & 0 & 107 \\ -43 & 10 & 0 & -110 & -107 & 0 \end{pmatrix} . \qquad (35)$$

The operator $\underline{H}^J_{\rm op}$ given by (33) has the following antisymmetrical part:

$$\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & -284 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -284 & 0 & 0 \\ 0 & 0 & 284 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 284 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} . \qquad (36)$$

Following the same technique used in I we calculate the ground-state energy, the orientation of the spin system, and the effective field at 0 °K.

The present calculation is carried out with the values of $J_1$ and $J_2$ given by Uryû,[11]

$$J_1/k = 0.0123\ {}^\circ\mathrm{K}\ , \qquad J_2/k = 0.0095\ {}^\circ\mathrm{K}\ , \qquad (37)$$

for the following cases:

$$J_1' = J_1/f\ , \quad J_2' = J_2/f\ , \qquad (38)$$

where $f$ assumes the values 1, 1.5, 2.0, 2.5, 3.0, $10^6$. The last value was used in order to check the calculations made in I which neglected exchange. The effective field at 0 °K in the tetragonal direction was found by Garrett to be 340 G and according to Miedema[4,5] the angle $\theta_M$ between the tetragonal axes and the direction of magnetization was found

TABLE II. Calculated values of the effective field $\vec{H}_{\rm eff}$, ground-state energy, and orientation $(\theta_M, \phi)$ of the spins for four values of the exchange parameters $J_1'$ and $J_2'$ defined in Eq. (38). Garrett's experimental values are given in column 8. The parameter $f$ is defined by Eq. (38).

| | $f=1$ | $f=1.5$ | $f=2.0$ | $f=2.5$ | $f=3.0$ | $f=10^6$ | Expt. |
|---|---|---|---|---|---|---|---|
| $H_{\rm eff}$(G) | 666 | 491 | 406 | 357 | 325 | 178 | 340[a] |
| Ground-state energy (cm$^{-1}$) | −0.1476 | −0.12027 | −0.1073 | −0.0999 | −0.09514 | 0.0744 | ... |
| $\vert\theta_M\vert$ | 10° | 4° | 2° | 0° | 2° | 11° | 10°[b] |
| $\phi$ | 15° | 17° | 17° | 18° | 19° | 21° | ... |

[a]From Reference 3. [b]From Reference 5.

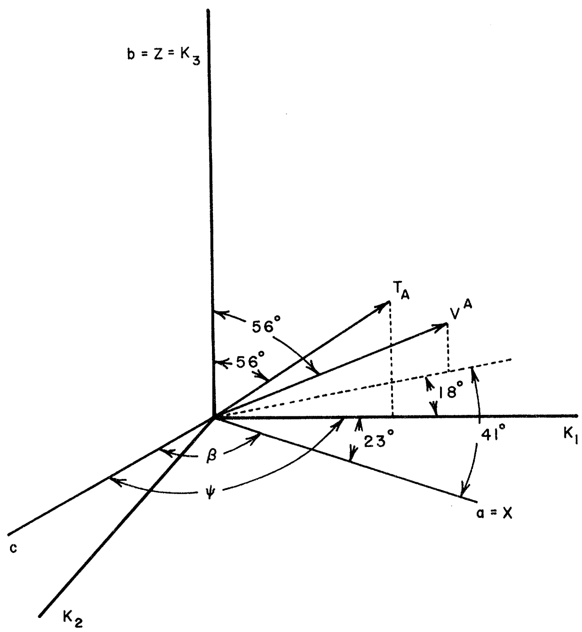


FIG. 3. Spin orientation at 0 °K including the dipole-dipole, hyperfine, and exchange interactions. Only spin type $A$ is shown. From the figure, $\theta_M = (56° - 56°) = 0°$ and $\phi = 18°$.

to be 10°. Uryû[10,11] defined the angle $\phi$ as the angle between the plane in which the spin lies and the $k_1 k_3$ plane and calculated it to be $\phi = 15°$. Our calculated values are given in Table II and Fig. 3.

## VI. DISCUSSION

There are three main criteria which may be employed to evaluate the merit of a theoretical calculation of the type presented here. They are the effective field $\vec{H}_{eff}$, the Nêel temperature $T_N$, and the angles of orientation. The calculated values of these three parameters for various magnitudes of $f$ were compared with experiment. The use of Uryû's exchange parameters $J_1$ and $J_2$ corresponding to the $f = 1$ case in column 2 of Table II provides an effective field of 637 G which was much higher than Garrett's experimental value of 340 G, which is given in column 8 of this table. In addition, the transition temperature $T_N$ calculated from the ground-state energy in column 2 is higher than 0.10 °K, which exceeds the experimental value of 0.084 °K. The actual method employed for calculating $T_N$ involves a complex iterative procedure, so the details are being reserved for a separate publication. The $f = 2.5$ case shown in column 5 gives an effective field of 357 G which is in fairly close agreement with Garrett's experimental value. In addition, the transition temperature calculated for $f = 2.5$ was close to the experimental value as well as the relation given in Eq. (4).

As Table II indicates, the angle $\theta_M$ is very little affected by the exchange, and in addition it is subject to a rather large experimental error. However, the spin system remains ferromagnetic in the $z$ direction and antiferromagnetic in the $xy$ plane for all ranges of $f$ values. Therefore, very little weight was given to the orientation in selecting the optimum value of $f$.

The antisymmetrical parts of the operators $\underline{H}^D_{op}$ and $\underline{H}^J_{op}$ given in Eqs. (34) and (35) determine the tilt of the spins. The hyperfine and dipole-dipole interactions alone tilt the spins to the $ac$ plane by $\theta_M = 11°$, as shown in Fig. 2. When the effect of exchange is included, the matrix elements of Eq. (35) are opposite in sign to their counterparts in Eq. (34), and the net effect is to reduce the angle $\theta_M$ to zero, as shown on Fig. 3.

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