

Low-Temperature Spin Orientation in Cobalt Tutton's Salt*

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The spin orientation of the Co^{+2} ions in $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was calculated for the minimum-energy state. First an effective magnetic field arising from the dipolar interaction was computed, and this was employed in the spin Hamiltonian to determine the energy of the cobalt Zeeman and hyperfine interactions. The latter was comparable to the dipolar energy, which complicated the computation. It was found that the spin system becomes antiferromagnetic below the estimated Néel temperature of 0.10°K . The spin orientations are given and shown to correspond to the magnetic space group $P2_1/a'$. The results are in general agreement with the experiment of Miedema, Postma, and Huiskamp.

INTRODUCTION

THE spin orientation configuration of magnetic dipole lattices at very low temperatures has been calculated by Luttinger and Tisza¹ (1946) and by Daniels and Felsteiner² (1964). The former authors treated the case of isotropic dipoles on cubic lattices, the latter treated the case of cerium magnesium nitrate, in which the lattice is trigonal and the g tensor of the magnetic ions is anisotropic. The method used by these authors was to assume that the magnetic ions form a superlattice. Luttinger and Tisza assumed that for the cubic lattices, the magnetic unit cell had twice the linear dimension of the chemical unit cell. The orientations of each of the dipoles in the unit cell are thus independent variables which describe the configurations of the dipoles in the whole crystal. From the orientations of the dipoles, it is possible to calculate the magnetic field produced at each of the dipoles by all the other dipoles in the crystal. The total interaction energy is the sum of the energy of each of the dipoles in the magnetic field $\sum_i \mathbf{u}_i \cdot \mathbf{H}_i$ and the low-temperature configuration is that for which this expression is a minimum. In all of these calculations, the magnetic dipoles were ions without hyperfine interactions. The purpose of this paper is to make a similar calculation for a magnetic salt in which the ions have a hyperfine interaction whose magnitude is comparable with the dipole-dipole interaction. In this case, the energy of the ion in the local field is not given by an expression as simple as $\mathbf{u} \cdot \mathbf{H}$. The procedure adopted is to treat the dipole-dipole interaction as equivalent to a local magnetic field as before. This field is inserted into the spin Hamiltonian for the ion, which is then diagonalized. The lowest eigenvalue is the energy of the ion, and the corresponding eigenvector describes the state of the ion. A self-consistent solution is then sought, in which the state of the ions obtained by

diagonalizing the spin Hamiltonian and choosing the lowest-energy state coincides with the state assumed for the calculation of the internal magnetic field. Since it is not possible to obtain an analytic expression for the energy of the ion in the local field, this self-consistent solution is sought by an iterative procedure, starting from an approximation to the configuration of lowest energy. It is expected that the configuration to which the iteration converges is, in fact, the lowest-energy configuration consistent with the assumptions that each ion is represented by its quantum-mechanical state, and that the magnetic interaction can be represented by an effective magnetic field.

In this paper we consider the Tutton's salt $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ which has an anisotropic g factor and a hyperfine term $\mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$ that is the same order of magnitude as the dipolar energy. As a result the latter two terms must be taken into account explicitly. This is a logical extension of the work of Daniels and Felsteiner which was for the case of a crystal with an anisotropic g factor with $I=0$.

In this salt there is a good reason to believe that the lowest-energy configuration is one in which the spin of each ion has a component in the direction of the positive b axis. Magnetic interaction causes the spin direction to rotate a few degrees towards the ac plane. The configuration, in which every spin has a component along the negative b axis, obtained by reflecting the original spin configuration in the ac plane, is also a configuration of lowest energy degenerate with the first one. The evidence for this conjecture lies in the low-temperature measurements made on this salt by the angular distribution of γ rays³ and by magnetic susceptibility.⁴

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¹ J. M. Luttinger and L. Tisza, *Phys. Rev.* **70**, 954 (1946).

² J. M. Daniels and J. Felsteiner, *Can. J. Phys.* **42**, 1469 (1964).

³ A. R. Miedema, H. Postma, and W. J. Huiskamp, *Proceedings of the Tenth International Conference on Refrigeration, Copenhagen, 1959*, p. 198 (unpublished).

⁴ A. R. Miedema, J. van den Broek, H. Postma, and W. J. Huiskamp, *Physica* **25**, 1177 (1959).

STRUCTURE AND MAGNETIC PROPERTIES

The solid compound $\text{Co}(\text{SO}_4) \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ is a Tutton's salt, and its symmetry and structure are well known. The space group $C_{2h}^5, P_{2_1}/a$ has a monoclinic unit cell with the dimensions⁵

$$\begin{aligned} a_0 &= 9.32 \text{ \AA}, \\ b_0 &= 12.51 \text{ \AA}, \\ c_0 &= 6.24 \text{ \AA}, \\ \beta &= 106.56^\circ, \end{aligned}$$

and with the symmetry axis orientations of the cobalt oxygen octahedra

$$\alpha = 34^\circ, \quad \psi = 130^\circ,$$

as defined below. There are two Co^{+2} ions per unit cell, type A at the position 000 and type B at the position $\frac{1}{2} \frac{1}{2} 0$, as shown in Fig. 1. All of the other atoms are located at general positions. Each Co^{+2} ion is surrounded by a distorted octahedron of water molecules with an axis of symmetry T_A and T_B for each sublattice, respectively. In Fig. 2 are shown these axes displaced to the origin and the angles and projections that will be used in this paper.

The Co^{+2} ion is in the $3d^7, {}^3F$ spectroscopic ground state with the total spin $S = \frac{3}{2}$, but in a magnetic problem the effective spin $S = \frac{1}{2}$ is employed. This considerably simplifies the labor involved in the present calculation. The nuclear spin $I = \frac{7}{2}$ gives rise to eight hyperfine components in the electron-spin resonance spectrum. The g factor and hyperfine coupling constant A of each Co^{+2} ion are given by Bleaney and Ingram⁶ as

$$\begin{aligned} g_{11} &= 6.45, & g_1 &= 3.06, \\ A_{11} &= 0.0245 \text{ cm}^{-1}, & A_1 &= 0.0020 \text{ cm}^{-1}. \end{aligned}$$

CLASSICAL TREATMENT AND DIPOLAR INTERACTION

In order to calculate the configuration of minimum interaction energy we start by assuming that the only interaction is dipolar. Following Daniels's notation⁷ we

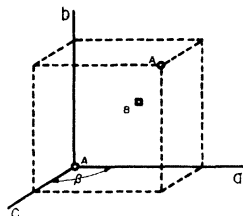


FIG. 1. Unit cell for $\text{Co}(\text{SO}_4)(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ showing Co^{+2} ions at two A sites (000), (111) and one B site ($\frac{1}{2} \frac{1}{2} 0$). Unit cell parameters are $a_0 = 9.32 \text{ \AA}$, $b_0 = 12.51 \text{ \AA}$, $c_0 = 6.24 \text{ \AA}$, and $\beta = 106.56^\circ$.

⁵ W. Hofmann, Z. Krist. **78**, 279 (1931); **82**, 323 (1932).

⁶ B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A208**, 143 (1951).

⁷ J. M. Daniels, Proc. Phys. Soc. (London) **66**, 673 (1953).

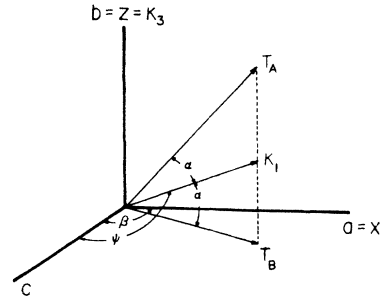


FIG. 2. Laboratory system x, y, z and crystallographic a, b, c axes for cobalt Tutton's salt. The axial symmetry directions of the two cobalt octahedra are indicated by T_A above the ac plane and by T_B below this plane for the A and B sites, respectively. They each have the projection k_1 in the ac plane. This projection makes the angle α with T_A and T_B , respectively, and ψ with the c axis.

write the dipole-dipole interaction energy W_{ij} between two ions i and j in tensor notation

$$W_{ij} = P_{ij\alpha\beta} \sigma_{i\alpha} \sigma_{j\beta}, \quad (1)$$

where Latin letters denote position, while Greek letters refer to the coordinates x, y, z , the σ are the Pauli matrices, and $P_{ij\alpha\beta}$ is defined as

$$P_{ij\alpha\beta} = \frac{1}{4} \beta^2 (g_{i\epsilon\alpha} g_{j\epsilon\beta} / r_{ij}^3 - 3g_{i\alpha\lambda} g_{j\lambda\beta} r_{ij\lambda} r_{ij\delta} / r_{ij}^5). \quad (2)$$

We follow the Einstein convention about the summation of repeated indices. The quantities $P_{ij\alpha\beta}$ constitute elements of the product of three matrices $[\mathbf{G}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{G}_j]$, where \mathbf{G}_i contains the elements g_i , and where \mathbf{D}_{ij} contains the diagonal elements $(r_{ij}^2 - 3r_{ij\alpha}^2) / r_{ij}^5$ and off-diagonal elements $-3r_{ij\alpha} r_{ij\beta} / r_{ij}^5$. More explicitly,

$$\mathbf{G}_i = \begin{pmatrix} g_{ixx} & g_{ixy} & g_{ixz} \\ g_{iyx} & g_{iyy} & g_{iyz} \\ g_{izx} & g_{izy} & g_{izz} \end{pmatrix}, \quad (3)$$

$$\mathbf{D}_{ij} = \frac{1}{r_{ij}^5} \begin{pmatrix} r_{ij}^2 - 3x_{ij}^2 & -3x_{ij}y_{ij} & -3x_{ij}z_{ij} \\ -3x_{ij}y_{ij} & r_{ij}^2 - 3y_{ij}^2 & -3y_{ij}z_{ij} \\ -3z_{ij}x_{ij} & -3z_{ij}y_{ij} & r_{ij}^2 - 3z_{ij}^2 \end{pmatrix}. \quad (4)$$

This allows us to write

$$W_{ij} = \frac{1}{4} \beta^2 \sigma_i \cdot (\mathbf{G}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{G}_j) \cdot \sigma_j. \quad (5)$$

The total interaction energy W_i of one ion with all the other ions in the lattice is obtained by summing Eq. (5):

$$W_i = \sum_{j \neq i} W_{ij}. \quad (6)$$

For a crystal with two sublattices A and B, the summation of Eq. (6) may be divided into a summation over each sublattice. For example, if i is on sublattice A, then

$$W_i = \sum_{j \neq i} W_{ij}^{AA} + \sum_j W_{ij}^{AB}, \quad (7)$$

where W_{ij}^{AB} is the dipolar interaction energy of the i th

TABLE I. Values of the sublattice sums used to determine the matrix elements $\sum_j D_{ij}^{AA} = \sum_j D_{ij}^{BB}$ and $\sum_j D_{ij}^{AB}$.^a

Sub-lattice	$\sum (3z^2 - r^2)/r^5$	$\sum (x^2 - y^2)/r^5$	$\sum xy/r^5$	$\sum xz/r^5$	$\sum yz/r^5$
$\left. \begin{matrix} AA \\ BB \end{matrix} \right\}$	-0.011046	-0.004631	0.001526	0	0
AB	0.008296	0.001213	0.000276	0	0

^a The summations were made inside a sphere of radius 150 Å; in addition, the values were calculated between the 150 Å radius and a 200 Å radius. The contribution of the points between the two radii is less than 0.5%.

ion of sublattice A with the j th ion of sublattice B . It is convenient to use 6×6 matrices to handle the two-sublattice problem, where

$$\mathbf{G}_i = \begin{pmatrix} \mathbf{G}_{i^A} & 0 \\ 0 & \mathbf{G}_{i^B} \end{pmatrix}, \quad (8)$$

$$\mathbf{D}_{ij} = \begin{pmatrix} \mathbf{D}_{ij}^{AA} & \mathbf{D}_{ij}^{AB} \\ \mathbf{D}_{ij}^{AB} & \mathbf{D}_{ij}^{BB} \end{pmatrix}, \quad (9)$$

and the appropriate superscripts may be added to the matrix elements of Eqs. (3) and (4) to designate the sublattices. This allows us to formulate and sum Eq. (6) in terms of 6×6 matrices for \mathbf{G} and \mathbf{D} :

$$W = \frac{1}{4}\beta^2 \boldsymbol{\sigma} \cdot (\mathbf{G} \cdot \mathbf{D} \cdot \mathbf{G}) \cdot \boldsymbol{\sigma}, \quad (10)$$

since \mathbf{G}_j and $\boldsymbol{\sigma}_j$ are the same for all j on a given sublattice.

$$\sum_j \mathbf{D}_{ij} \cdot \mathbf{G}_j \cdot \boldsymbol{\sigma}_j = \left(\sum_j \mathbf{D}_{ij} \right) \cdot \mathbf{G}_j \cdot \boldsymbol{\sigma}_j. \quad (11)$$

The axially symmetric g value is diagonal in the tetragonal system with g_{11} along \mathbf{T}_A (or \mathbf{T}_B). Equation (5), on the other hand, is expressed in the lab system where the summation is much easier to evaluate. As a result we need two transformations of g , one that goes from the tetragonal system \mathbf{T}_A to the lab system \mathbf{T}_L , and another that goes from the tetragonal system \mathbf{T}_B to the laboratory system. These are denoted, respectively, by \mathbf{R}_A^\dagger and \mathbf{R}_B^\dagger , where the dagger means transpose conjugate. It is easy to calculate \mathbf{R}_A and \mathbf{R}_B , and following Fig. 2, we have

$$\mathbf{R}_A = \mathbf{R}_y^\alpha \mathbf{R}_z^{\psi-\beta}, \quad (12)$$

$$\mathbf{R}_B = \mathbf{R}_y^{-\alpha} \mathbf{R}_z^{\psi-\beta}, \quad (13)$$

where $\alpha = 34^\circ$ and $\psi = 130^\circ$. A 6×6 matrix \mathbf{R}_L with the upper left-hand 3×3 block is equal to \mathbf{R}_A and the lower

right-hand 3×3 block constituting \mathbf{R}_B transforms each sublattice from the same laboratory system to its particular tetragonal coordinate system:

$$\mathbf{R}_L = \begin{pmatrix} \mathbf{R}_A & 0 \\ 0 & \mathbf{R}_B \end{pmatrix}. \quad (14)$$

This matrix may be employed to transform each 3×3 part of \mathbf{G} to the laboratory system. Both \mathbf{G}^A and \mathbf{G}^B are diagonal in their respective tetragonal coordinate systems. It is most convenient to carry out the calculations in the laboratory system which is defined in terms of the crystallographic axes. There are only two types of dipole matrix, namely, $\mathbf{D}^{AA} = \mathbf{D}^{BB}$ and $\mathbf{D}^{AB} = \mathbf{D}^{BA}$, since the two sites are related to each other by a symmetry operation. To calculate the matrix \mathbf{D} we need only to know sums over the quantities $(3z^2 - r^2)/r^5$, $(x^2 - y^2)/r^5$, xy/r^5 , xz/r^5 , and yz/r^5 , since proper linear combinations of these produce all nonzero matrix elements in \mathbf{D} . The summations are given in Table I.

Using the 6×6 matrices \mathbf{G} and \mathbf{D} in the laboratory system we can calculate matrix \mathbf{a} as

$$\mathbf{a} = \frac{1}{4}\beta^2 (\mathbf{G} \cdot \mathbf{D} \cdot \mathbf{G}), \quad (15)$$

and then diagonalize it to obtain the six eigenvalues λ' and eigenvectors V' . The results are shown in Table II. The six eigenvectors not only form an orthonormal set (weak constraint) but they obey the orthonormality condition (strong constraint) within each sublattice:

$$V_{xi}{}^A V_{xj}{}^A + V_{yi}{}^A V_{yj}{}^A + V_{zi}{}^A V_{zj}{}^A = \frac{1}{2} \delta_{ij}, \quad (16)$$

with a similar expression for the B sublattice.

The interaction energy W_{ij} has been expressed in terms of two interacting magnetic moments \mathbf{u}_1 and \mathbf{u}_2 . This may be looked upon as the interaction of one of the magnetic moments with the magnetic field \mathbf{H}_{0p} produced at its site by the other moment $\mathbf{u}_1 \cdot \mathbf{H}_2 = \mathbf{u}_2 \cdot \mathbf{H}_1$. The operator \mathbf{H}_{0pj} may be looked upon as the magnetic field operator at ion j due to all of the other magnetic moments in the lattice. Hence, it is given by

$$\mathbf{H}_{0p} = \frac{1}{2}\beta \mathbf{D} \cdot \mathbf{G}, \quad (17)$$

where as usual the subscript j is dropped for convenience. The magnetic field \mathbf{H}_L corresponding to the lowest energy level λ_6' is the following six-component vector:

$$\mathbf{H}_L = \mathbf{H}_{0p} \cdot \mathbf{V}_6'. \quad (18)$$

This magnetic field vector is easily transformed from its

TABLE II. Eigenvalues λ' and eigenvectors V_j' for the dipolar matrix \mathbf{a} .

Level V_j'	λ' (cm^{-1})	$V_{xi}{}^A$	$V_{yi}{}^A$	$V_{zi}{}^A$	$V_{xi}{}^B$	$V_{yi}{}^B$	$V_{zi}{}^B$
V_1'	0.040	0.383	-0.045	0.921	0.383	-0.045	-0.921
V_2'	0.008	0.816	-0.420	-0.366	0.816	-0.420	0.366
V_3'	0.005	0.136	-0.245	0.960	-0.136	0.245	0.960
V_4'	0.000	-0.885	0.406	0.228	0.885	-0.406	0.228
V_5'	-0.015	0.405	0.906	-0.122	0.405	0.906	0.122
V_6'	-0.034	0.446	0.881	0.161	-0.446	-0.881	0.161

present lab system to the coordinate system where the g factors are diagonal by means of the matrix \mathbf{R}_L defined above, to give

$$\mathbf{H} = \mathbf{R}_L \cdot \mathbf{H}_L. \quad (19)$$

Thus far we have treated the problem classically. To find the spin alignment it will be necessary to employ quantum mechanics, using this magnetic field \mathbf{H} in the spin Hamiltonian where g is diagonal.

QUANTUM TREATMENT AND HYPERFINE INTERACTION

In the previous section we found the effective magnetic field arising from the dipole-dipole interaction of the surrounding spins. Now we will proceed to solve the spin Hamiltonian using this field \mathbf{H} as the applied magnetic field acting on the electronic spins. The Hamiltonian in tensor notation⁸ is

$$H = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}. \quad (20)$$

For the present Tutton salt crystal we have axial symmetry with the specific parameters

$$H = \beta [g_x(S_x H_x + S_y H_y) + g_z S_z H_z] + A_{11}(S_x I_x + S_y I_y) + A_{11} S_z I_z. \quad (21)$$

The magnitudes of g_{11} , g_1 , A_{11} , and A_1 were given above. The effective spin $S = \frac{1}{2}$ is employed, although the actual spin for the $\text{Co}^{+2}3d^7\ ^3F$ ground state is $\frac{3}{2}$.

The Hamiltonian (21) is complex, and to simplify it we apply the further rotation \mathbf{R}_z^θ ,

$$\mathbf{R}_z^\theta = \begin{pmatrix} \mathbf{R}_z^{\theta_A} & 0 \\ 0 & \mathbf{R}_z^{\theta_B} \end{pmatrix}, \quad (22)$$

where the 3×3 matrices $\mathbf{R}_z^{\theta_A}$ and $\mathbf{R}_z^{\theta_B}$ rotate about the tetragonal axes through the angles

$$\begin{aligned} \theta_A &= \tan^{-1}(H_y^A/H_x^A), \\ \theta_B &= \tan^{-1}(H_y^B/H_x^B). \end{aligned} \quad (23)$$

The total rotation in the lab system is thus

$$\mathbf{R} = \mathbf{R}_z^\theta \mathbf{R}_L. \quad (24)$$

The diagonalization of the Hamiltonian (21) will produce 16 eigenvectors ψ_j and 16 eigenvalues λ_j since there is a degeneracy of $(2S+1)(2I+1) = 16$. The polarization in the ground state with the eigenvalue λ_{16} and associated eigenvector ψ_{16} is

$$P_\alpha = \langle \psi_{16} | S_\alpha | \psi_{16} \rangle, \quad (25)$$

where $\alpha = x, y, z$ and the three components P_α may be calculated for each sublattice.

Since the hyperfine coupling constant \mathbf{A} is the same order of magnitude as the Zeeman term, the practical

calculations were carried out in several stages in a self-consistent manner. First, the equations were solved for $A_{11} = A_{11} = 0$ to check the eigenvalues and polarization. Then Eq. (25) was computed to obtain the six-component polarization vector \mathbf{P}' . This was compared with \mathbf{V}_6' , which is in the lab system, through the relation

$$\mathbf{V}_6'' = \mathbf{R}_L \mathbf{P}'. \quad (26)$$

This vector \mathbf{V}_6'' is used in Eq. (18) to compute a new magnetic field for use in the Hamiltonian. With this new field \mathbf{H}'' and the values $\frac{1}{10}A_1$ and $\frac{1}{10}A_{11}$ for the hyperfine term, the computation process was repeated. The new minimum eigenvalue has an associated eigenvector which was used to calculate a new polarization called \mathbf{P}'' . The new polarization \mathbf{P}'' gave a new vector $\mathbf{V}_6''' = \mathbf{R}_L \mathbf{P}''$, which provided the magnetic field $\mathbf{H}''' = \mathbf{H}_{0p} \mathbf{V}_6'''$ for use in the next cycle of solving the Hamiltonian equation. The process was repeated iteratively until the same polarization vector was obtained after two consecutive iterations. Then the values of A_1 and A_{11} were increased to 20% of their true values, and the process was repeated using the final or self-consistent values of the 10% A calculations for the initial iteration. At each step of increasing A_1 and A_{11} by 10% the calculations converged rapidly to a self-consistent answer. The final-ground-state eigenvalue λ and polarization components V_i are listed in Table III. Figure 3 shows the orientation of the polarization vectors \mathbf{V}^A and \mathbf{V}^B and the corresponding tetragonal axes \mathbf{T}^A and \mathbf{T}^B .

Finally, we list the following components for the state vector of the cobalt ions in their lowest-energy state $|\psi_{16}\rangle$ (spin types A and B); the first quantum number corresponds to the electron spin and the second

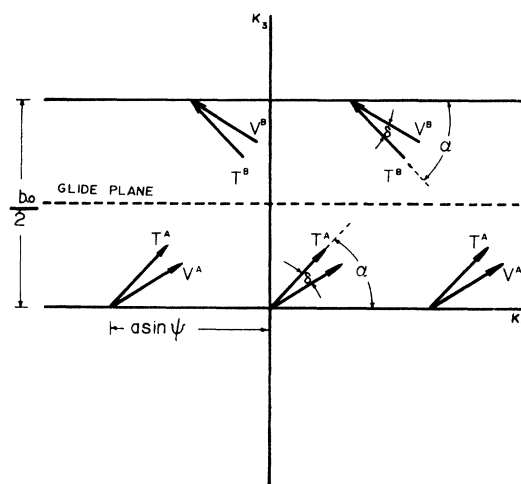


FIG. 3. Normal projections onto the k_1 - k_2 plane of the eigenvectors V and tetragonal axis vectors T with their origins at the cobalt lattice sites. The horizontal glide plane between the sites is at $k_2 = \frac{1}{2}b_0$. The A-site projections occur along $k_2 = 0$ at the positions $k_1 = 0, \pm a \sin \psi, \pm 2a \sin \psi, \dots$, while the B-site projections are situated at $k_2 = \frac{1}{2}b_0$ and the sites $k_1 = \pm \frac{1}{2}a \sin \psi, \pm \frac{3}{2}a \sin \psi, \dots$

⁸ K. D. Bowers and J. Owen, Rept. Progr. Phys. **18**, 304 (1955).

TABLE III. Column 2 gives the minimum-energy eigenvectors V^A and V^B for the cobalt spins. These values were determined from the entire Hamiltonian, including the dipolar, hyperfine, and Zeeman terms. The minimum-energy eigenvalue is $\lambda = -0.06776 \text{ cm}^{-1}$. The components of the dipolar field at the cobalt site are given in column 3 for the dipole-dipole interaction H_{dd} alone, and in column 4 for the combination dipolar-hyperfine interaction H_{ddA} .

Eigenvector component	Eigenvector value	H_{dd} (G)	H_{ddA} (G)
V_x^A	0.679	-74	-70
V_y^A	0.613	-355	-330
V_z^A	0.403	24	39
V_x^B	-0.679	74	70
V_y^B	-0.613	355	330
V_z^B	0.403	24	39

to the nuclear spin:

$ \psi_{16}\rangle$ (spin type A)	$ \psi_{16}\rangle$ (spin type B)
0.0000 $ \frac{1}{2}, +\frac{7}{2}\rangle$	0.1664 $ \frac{1}{2}, +\frac{7}{2}\rangle$
0.0000 $ \frac{1}{2}, +\frac{5}{2}\rangle$	-0.0098 $ \frac{1}{2}, +\frac{5}{2}\rangle$
0.0000 $ \frac{1}{2}, +\frac{3}{2}\rangle$	0.0005 $ \frac{1}{2}, +\frac{3}{2}\rangle$
0.0000 $ \frac{1}{2}, +\frac{1}{2}\rangle$	0.0000 $ \frac{1}{2}, +\frac{1}{2}\rangle$
-0.0001 $ \frac{1}{2}, -\frac{1}{2}\rangle$	0.0000 $ \frac{1}{2}, -\frac{1}{2}\rangle$
0.0024 $ \frac{1}{2}, -\frac{3}{2}\rangle$	0.0000 $ \frac{1}{2}, -\frac{3}{2}\rangle$
-0.0525 $ \frac{1}{2}, -\frac{5}{2}\rangle$	0.0000 $ \frac{1}{2}, -\frac{5}{2}\rangle$
0.9846 $ \frac{1}{2}, -\frac{7}{2}\rangle$	0.0000 $ \frac{1}{2}, -\frac{7}{2}\rangle$
0.0000 $ \frac{1}{2}, +\frac{7}{2}\rangle$	0.9846 $ \frac{1}{2}, +\frac{7}{2}\rangle$
0.0000 $ \frac{1}{2}, +\frac{5}{2}\rangle$	-0.0525 $ \frac{1}{2}, +\frac{5}{2}\rangle$
0.0000 $ \frac{1}{2}, +\frac{3}{2}\rangle$	0.0024 $ \frac{1}{2}, +\frac{3}{2}\rangle$
0.0000 $ \frac{1}{2}, +\frac{1}{2}\rangle$	-0.0001 $ \frac{1}{2}, +\frac{1}{2}\rangle$
0.0000 $ \frac{1}{2}, -\frac{1}{2}\rangle$	0.0000 $ \frac{1}{2}, -\frac{1}{2}\rangle$
0.0005 $ \frac{1}{2}, -\frac{3}{2}\rangle$	0.0000 $ \frac{1}{2}, -\frac{3}{2}\rangle$
-0.0098 $ \frac{1}{2}, -\frac{5}{2}\rangle$	0.0000 $ \frac{1}{2}, -\frac{5}{2}\rangle$
0.1664 $ \frac{1}{2}, -\frac{7}{2}\rangle$	0.0000 $ \frac{1}{2}, -\frac{7}{2}\rangle$

DISCUSSION

The eigenvectors V^A and V^B of Table III give the directions of the magnetization vectors arising from the

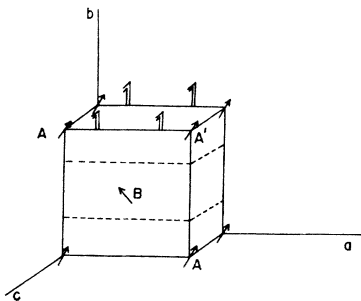


FIG. 4. Magnetic unit cell of cobalt Tutton's salt showing seven A-type spins and one B-type spin. Dashed lines indicate the two glide planes and four vertical screw axes are also indicated. For the magnetic ground state the spin orientations may be either as shown, or with all of the spins reversed in direction.

two types of cobalt spins in their magnetic ground states. These directions were determined from the entire spin Hamiltonian, including the Zeeman, dipolar, and hyperfine interactions. The magnetization directions in the absence of hyperfine interactions are given in Table II for the various energy states. The ground state -0.06776 cm^{-1} including hyperfine interactions is lower by 0.03412 cm^{-1} than that without this interaction, which indicates that the hyperfine term stabilizes the magnetic energy at low temperature, and thereby raises the Néel point.

The Néel temperature T_N may be estimated by equating the eigenvalue -0.06776 cm^{-1} of the magnetic ground state to the thermal energy kT :

$$T_N = |\lambda|/k = 0.10^\circ\text{K}.$$

This agrees well with the value $T_N \sim 0.08^\circ\text{K}$ reported by Miedema *et al.*^{3,4}

Below the Néel temperature the spins on the two sublattices align oppositely relative to their respective tetragonal axes \mathbf{T}_A and \mathbf{T}_B . The tetragonal directions are related by the fact that the space group has a screw axis s along the b direction and glide planes p perpendicular to the b direction, as shown in Fig. 4. In addition, it has centers of inversion i at the cobalt sites shown on this figure. In the magnetic space group associated with the cobalt magnetic moments, the screw axes remain so, but the glide plane p becomes a glide-plane spin-reversal symmetry operation tp , where t is the time-reversal operator which inverts spin directions without affecting the space coordinates. The inversion operation i must be accompanied by a spin-reversal t to leave the magnetic lattice unchanged. According to these rules spin B of Fig. 4 transforms to spin A by a translation $\frac{1}{2}a$, a reflection in the lower glide plane, and a spin reversal. Spin B transforms to spin A' by means of a translation of $\frac{1}{2}b$ and a rotation of π about the screw axis s . These two sets of operations tp and s interchange spins between the two sublattices, while ti interchanges them within the sublattices. This magnetic space group or Shubnikov group may be designated $P2_1/a'$ where a' indicates that the glide plane is associated with the time-inversion operation, while the screw axis 2_1 is not.

The nature of the low-temperature magnetization may be elucidated by considering its projection in a plane containing the tetragonal axes \mathbf{T}_A and \mathbf{T}_B and the crystallographic b axes. Figure 2 shows the vector T_B pointing out from its atomic site $\frac{1}{2}\frac{1}{2}0$ [radius vector $(\frac{1}{2}a, \frac{1}{2}b, 0)$] and displaced so it points down from the origin while retaining its magnitude and direction. It will be convenient to employ the orthogonal coordinate system whereby k_1 is the bisector of the \mathbf{T}_A - \mathbf{T}_B angle, k_3 is coincident with b and z , and k_2 is in the ac plane perpendicular to k_1 and k_3 , as shown in Fig. 2.

The orientations of the \mathbf{T}_A and \mathbf{T}_B directions in the k_1 - k_3 plane, as well as the projections of the V^A and V^B

directions in this plane, are shown in Fig. 3. Here the actual-site vectors are projected normally in this plane and the glide plane is indicated. Figures 3, 5, and 6 show that the magnetization \mathbf{V}^A and \mathbf{V}^B is antiferromagnetically aligned in the k_1 and k_2 directions, and ferromagnetically aligned in the k_3 or b -axis direction. This is in agreement with the experimental results of Miedema *et al.*,^{3,4} and is a consequence of the symmetry of the magnetic space group $P2_1/a'$.

It will be of interest to clarify the spatial orientation of the vector \mathbf{V}^A in terms of the polar angle θ between \mathbf{V}^A and the $Z=k_3$ axis, and the azimuthal angle φ between the projection of \mathbf{V}^A on the xy plane and the x direction. Miedema *et al.* determined a polar angle $\theta=62^\circ$ for the nuclear-spin magnetization by angular correlation measurements,³ and determined the polar angle $\theta=66^\circ$ for the electron spins by magnetic susceptibility.⁴ Since the axial component of the hyperfine interaction is dominant ($A_{11}\gg A_{\perp}$), it is expected that there should be little difference between the directions of the magnetization arising from the electronic and nuclear spins. The possibility of the individual magnetizations being out of the k_2k_3 plane was not detected by Miedema *et al.*, so they reported $\varphi=23^\circ$ relative to x and $\varphi_k=0^\circ$ relative to the $k_1k_2k_3$ coordinate system (cf. Fig. 6). Uryû calculated $\theta\sim 100^\circ$ and $\varphi_k\sim 11^\circ$. Our value of $\theta=66^\circ$ is in agreement with

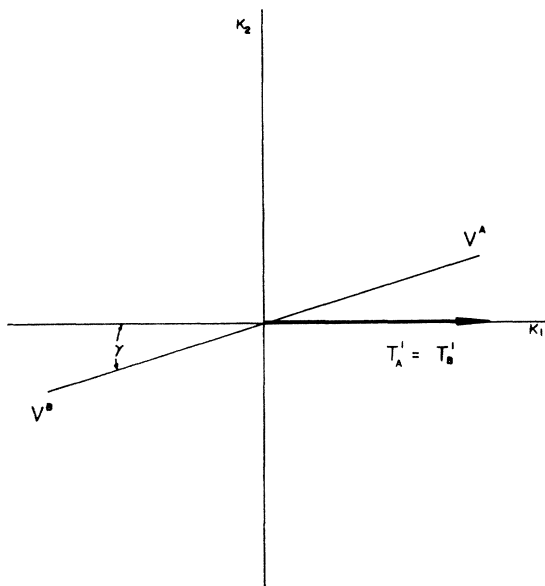


FIG. 5. Projections of the polarization vector directions \mathbf{V}^A and \mathbf{V}^B and the coincident tetragonal directions T_A and T_B on the k_1 - k_2 plane. The angle $\gamma=19^\circ$.

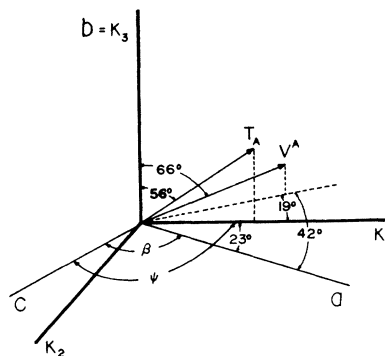


FIG. 6. Orientation of the axial crystal field direction T_A in the k_1 - k_3 plane, and the eigenvector V^A shown 19° azimuthal behind the k_1 axis with its indicated projection (----) on the k_1 - k_2 plane. The difference in the polar angle $\theta=56^\circ$ and 66° for T_A and V^A , respectively, is 10° , which is close to the value 6° reported by Miedema under the assumption that both T_A and V^A are in the k_1 - k_3 plane. The angles β and ψ are 107° and 130° , respectively. To simplify the drawing the k_2 axis was drawn in the negative direction toward the reader.

the measurements of Miedema *et al.*, and our value of $\varphi_k=19^\circ$ is not far from Uryû's value.⁹ Uryû's result for θ is, however, in disagreement with experiment.

In this paper the spin alignment of the cobalt electronic spins was determined by taking into account the dipolar interaction between the electronic spins and the hyperfine interaction with the cobalt nuclei. The calculations of Uryû take into account the dipolar and exchange interactions. We have been able to employ accurate values of the hyperfine coupling constant A , since they are well known from ESR results. Uryû, on the other hand, was forced to guess at the value of the exchange integral J since it has not been measured. Nakamura and Uryû¹⁰ estimated $J=0.013\text{ cm}^{-1}$, which is only half as large as A_{11} .

CONCLUSIONS

A method for calculating the minimum-energy orientation of a system of electronic spins under the action of an axially symmetric g factor and a hyperfine interaction of comparable magnitude has been presented. The method was employed to deduce the ground-state configurations of antiferromagnetic cobalt ions in Tutton's salt below their Néel temperature. The calculations made use of the known crystallographic and ESR data, and provided a magnetic structure in general agreement with the γ -ray angular correlation measurements.

⁹ N. Uryû, J. Phys. Soc. Japan **16**, 2139 (1961).

¹⁰ T. Nakamura and N. Uryû, J. Phys. Soc. Japan **11**, 760 (1956).