the symmetry at the vanadium site is less than cubic for $T > 160°K$, it is unlikely that the crystallographic transformation from rhombohedral to monoclinic symmetry will lead to a quadrupolar broadened V^{51} NMR line shape for $T < 160°K$. Thus, it is not inconsistent to conclude that V_2O_3 undergoes an antiferromagnetic transition at 160°K; and for temperatures less than 160°K, the V^{51} NMR would occur at higher frequencies (200–350 Mc/sec).

An estimate for the NMR linewidth δH for a nucleus of a paramagnetic ion has been given by Moriya[20] with the result

$$\delta H \simeq \left(\frac{2\pi}{3}\right)^{1/2} \frac{A^2 S(S+1)}{3\gamma\hbar^2\omega_e}, \tag{7}$$

where A is the hyperfine coupling constant, S the electron spin, γ the nuclear gyromagnetic ratio and ω_e is defined by

$$\omega_e^2 = \tfrac{2}{3}(J/\hbar)^2 Z S(S+1), \tag{8}$$

where Z is the number of neighbors and $-J$ is the antiferromagnetic exchange constant. The molecular field approximation gives a relationship between the exchange constant J and the Curie temperature θ as[6]

$$\frac{3k\theta}{2S(S+1)ZJ} \simeq 1. \tag{9}$$

From Eqs. (8) and (9), and taking $Z \simeq 6$,

$$\omega_e \simeq (\tfrac{1}{8})^{1/2}(k\theta)/\hbar \tag{10}$$

or for $|\theta| \simeq 600°K$, $\omega_e \simeq 3\times10^{13}\ \text{sec}^{-1}$. An estimate for the hyperfine coupling constant A can be made by combining the previously determined values of H_d^{hf} and μ_{eff} with the result $A \simeq 100\times10^{-4}\ \text{cm}^{-1}$. The line width δH is thus calculated from Eq. (7) to be

$$(\delta H)_{\text{calc}} \simeq 20\ \text{G} \tag{11}$$

which is in satisfactory agreement with the observed $\delta H \simeq 16$ G. For comparison, the dipolar linewidth in V_2O_3 is of the order of 3 G.

ACKNOWLEDGMENTS

The author wishes to thank C. Britz for experimental assistance and S. Geschwind, A. C. Gossard, and V. Jaccarino for many helpful discussions.

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Magnetic Properties of CoF_2

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CoF_2 is a simple two-sublattice antiferromagnet and has a rutile crystal structure. Each Co^{++} ion is surrounded by a rhombically distorted octahedron of fluorine anions and the crystal-field parameters are known from an analysis of infrared absorption measurements. A good description of a single Co^{++} system can be obtained in terms of a spin Hamiltonian with $S=\frac{3}{2}$. In this paper, an exchange Hamiltonian for the entire lattice is determined in which the only unknowns are the exchange parameters J_1 and J_2 describing interactions between nearest- and next-nearest-neighbor Co^{++} ions, respectively. The resulting intermediate coupling problem is attacked by spin-wave methods, introducing operators which represent deviations of spin from the molecular-field ground state. The parameters J_1 and J_2 are determined by calculating the antiferromagnetic resonance frequency and the temperature dependence of sublattice magnetization, and by fitting theory to experiment. We find that J_1 is very small and probably ferromagnetic. With the exchange Hamiltonian now completely determined, a molecular-field treatment is shown to reproduce closely the measured parallel and perpendicular magnetic susceptibilities in the temperature range 0 to 300°K (except in the immediate vicinity of the Néel temperature), and is used to discuss the nuclear magnetic resonance of Co^{59} in CoF_2.

1. INTRODUCTION

SOME years ago, an attempt was made by Nakamura and Taketa[1] to obtain a theoretical understanding of the somewhat unusual magnetic properties of the antiferromagnetic salt CoF_2. At that time, however, the experimental information was scant, consisting of little more than a knowledge of the magnetic structure of the crystal and some rather incomplete susceptibility data. Even so, they found it possible to obtain a qualitative explanation of the unusual features of the susceptibility curves and were able to demonstrate the origin of the large anisotropy which exists in the salt and to obtain some measure of the exchange interaction present. Since that time, a considerable amount of new experimental data has been obtained and we are now in a position where a more quantitative approach to the problem can be attempted.

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CoF_2 has the rutile crystal structure with cations on a body-centered tetragonal lattice. At low temperatures it exhibits a simple two-sublattice antiferromagnetic ordering in which all the spins align along the tetragonal c axis.[2] It has, therefore, exactly the same spin pattern and crystal structure as the much investigated and so-called "ideal" antiferromagnet MnF_2.[2–4] The reason why the magnetic properties of these two salts are so different centers around the fact that the ground state of a free Mn^{++} ion is an S state and is therefore almost completely free from the influence of the crystalline electric field, while the ground state of a free Co^{++} ion is an F state with orbital degeneracy which is partly or completely removed by such a field. Thus, whereas it is possible to write down immediately a spin Hamiltonian (the Heisenberg Hamiltonian) to represent the MnF_2 system, the spin Hamiltonian for CoF_2 must first be derived from a knowledge of the form of the crystalline electric field and it will thus contain crystal field parameters in addition to exchange parameters.

Experimental results concerning CoF_2 which have recently been obtained and are relevant to the present discussion include measurements of:

(1) The infrared absorption spectrum[5] consisting of several peaks in the 0.15–0.20-eV range;

(2) Single crystal magnetic susceptibilities both parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to the c axis[6] over the temperature range 0–300°K;

(3) Antiferromagnetic resonance frequencies[7] at very low temperatures;

(4) Variation of sublattice magnetization with temperature in the ordered state, by studying the magnetic resonance of the fluorine anion nuclei in the effective fields of the cation spins[8];

(5) Magnetic resonance of the cation nucleus (Co^{59}) itself[9];

(6) Electron spin resonance of Co^{++} in ZnF_2 and estimates of the principal g values for this case.[10]

Of particular interest are the properties in the spin-wave region. For the simpler case of MnF_2 it is now claimed[11–13] that spin-wave theories are able to give a very satisfactory quantitative description of the antiferromagnetic state right up to temperatures approaching the Néel point T_N (but see Jones and Jefferts[14]). Moreover, it would appear from these analyses that the comparison of spin-wave theory with experiment in these low-temperature regions provides perhaps the most accurate method for extracting information concerning exchange interactions which is presently available. It is the purpose of the present paper to show firstly that a simple spin-wave theory is able to describe the very low-temperature properties of CoF_2 in a satisfactory way, enabling estimates to be made of the exchange interactions which exist both between the same and opposite sublattices, and secondly to show that these same values of exchange enable a good agreement between theory and experiment to be obtained for the other properties about which we have any knowledge. In particular, we find that the exchange interaction between spins on the same sublattice has a value very small compared with the antiferromagnetic exchange between spins on opposite sublattices. In this respect, it seems as though CoF_2 and MnF_2 may well have similarities and, although the accuracy of theory obtained in this paper may not be sufficient to attach much weight to the exact value obtained for the smaller exchange, we find it to be ferromagnetic in sign (which is also the case for MnF_2).[12,15]

2. CRYSTAL FIELD THEORY

CoF_2 is a salt which exhibits the rutile crystal structure (Fig. 1). Each Co^{++} ion is surrounded by a distorted octahedron of F^- ions.[3] The lowest orbital state of the free Co^{++} ion (derived from the configuration $3d^7$) is ^4F. In the presence of a cubic crystalline field, this state splits into two orbital triplets and one singlet with the singlet highest.[16] For all but the most detailed of discussions it is customary to neglect at this stage the effect of the upper states and concentrate on the lowest orbital state alone. This twelvefold degenerate state (spin $S=\frac{3}{2}$) is split into six Kramers doublets by the combined effects of spin-orbit coupling and terms representing the distortion of the crystal field from cubic form. For CoF_2, this distortion has both axial and rhombic components and the perturbing Hamiltonian may be written as

$$\mathcal{H}=-\tfrac{3}{2}\lambda L\cdot S+\Delta(L_z^2-\tfrac{2}{3})+\Gamma(L_x^2-L_y^2)\,, \tag{2.1}$$

where the axes x, y, z, are indicated in Fig. 1; and where λ, Δ, Γ, are, respectively, the spin-orbit coupling constant, the axial crystalline field parameter, and the rhombic field parameter. The numerical factor $-\frac{3}{2}$ in the spin-orbit term arises because the matrix elements of the orbital angular momentum $\mathbf{L}$ between the three orbital states of the unperturbed level are the same as the matrix elements of $-\frac{3}{2}\mathbf{L}$ between the associated P functions (see, for example, Griffith).[17]

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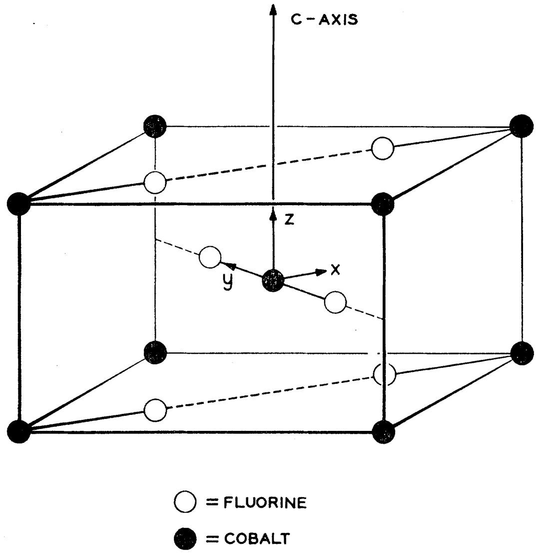

FIG. 1. The rutile crystal structure with axes x, y, z, as used in the text.

The perturbation problem has been investigated by Kamimura and Tanabe[18] who show that the absorption peaks observed by Newman and Chrenko[5] correspond to transitions within the ground state multiplet. They find that a quantitative agreement between theory and experiment may be obtained which allows the parameters in the perturbing Hamiltonian to be determined. They find, in particular, that $\lambda=-157\ \text{cm}^{-1}$ and that the lowest two Kramers doublets are separated in energy by 175 cm^{-1} and are removed from the remaining doublets by energies which are several times larger than this. It seems likely, therefore, that for temperatures in our range of interest (zero to 300°K) a good description of the system can be obtained by taking account of the two lowest doublets only, and we shall assume this to be the case. Using Eq. (2.1) together with a subsequent analysis, Kamimura[19] reports that the spin contribution to the g values of the lowest doublet are $g_x{}^s=4.55$, $g_y{}^s=1.98$, $g_z{}^s=3.08$.

We may now show that the above g^s-values and a doublet separation of 175 cm^{-1} may be obtained to a good approximation from an effective spin-$\frac{3}{2}$ Hamiltonian of the form

$$\mathcal{H}=\gamma(S_x{}^2-S_y{}^2)+\delta S_z{}^2\,, \tag{2.2}$$

where γ and δ are parameters to be determined below. The ability of a Hamiltonian of this form to describe the system is an indication of the validity of the assumption made by Nakamura and Taketa[1] that the lowest orbital level of Co^{++} in CoF_2 is nondegenerate and widely separated from the next in comparison with λ.

The Hamiltonian (2.2) may readily be diagonalized when we find eigenvalues $E_i{}^\pm$ and eigenfunctions $\psi_i{}^\pm$ as follows:

$$E_2{}^\pm=5\delta/4+(\delta^2+3\gamma^2)^{1/2}\,, \tag{2.3}$$

$$\psi_2{}^\pm=C_2|\tfrac{3}{2},\pm\tfrac{3}{2}\rangle-C_1|\tfrac{3}{2},\mp\tfrac{1}{2}\rangle\,, \tag{2.4}$$

$$E_1{}^\pm=5\delta/4-(\delta^2+3\gamma^2)^{1/2}\,, \tag{2.5}$$

$$\psi_1{}^\pm=C_1|\tfrac{3}{2},\pm\tfrac{3}{2}\rangle+C_2|\tfrac{3}{2},\mp\tfrac{1}{2}\rangle\,, \tag{2.6}$$

where

$$C_1/C_2=[\delta-(\delta^2+3\gamma^2)^{1/2}]/\sqrt{3}\gamma\,. \tag{2.7}$$

The matrix elements of S_x, S_y, S_z, within the ground doublet $\psi_1{}^\pm$ are therefore

$$S_x=ps_x\,,\quad S_y=qs_y\,,\quad S_z=rs_z\,, \tag{2.8}$$

where s_x, s_y, s_z are the (Pauli) matrices for an effective spin-$\frac{1}{2}$ operator $\mathbf{s}$, and where

$$p=2\sqrt{3}C_1C_2+2C_2{}^2\,, \tag{2.9}$$

$$q=2\sqrt{3}C_1C_2-2C_2{}^2\,, \tag{2.10}$$

$$r=3C_1{}^2-C_2{}^2\,. \tag{2.11}$$

If we use wave functions normalized to unity ($C_1{}^2+C_2{}^2=1$) we have only a single variable C_1/C_2 which we attempt to choose so that $p\approx\frac{1}{2}g_x{}^s=2.275$; $q\approx\frac{1}{2}g_y{}^s=0.99$; $r\approx\frac{1}{2}g_z{}^s=1.54$. We plot p, q, r, as functions of C_1/C_2 in Fig. 2. We find that when $C_1=1.36C_2$, the parameters are all within 4% of Kamimura's values. Writing $E_2-E_1=175\ \text{cm}^{-1}$, and using Eqs. (2.3), (2.5), and (2.7), we find the corresponding values for the spin Hamiltonian parameters γ and δ to be

$$\gamma=-48.2\ \text{cm}^{-1}\,,\quad \delta=-26.3\ \text{cm}^{-1}\,. \tag{2.12}$$

But we can do even better than this. Thus, for example, some properties depend dominantly only on one or two of the ground doublet-spin matrix elements, and it is possible to choose γ and δ so that the matrix elements concerned agree exactly (or extremely closely) with those obtained from a treatment including all six

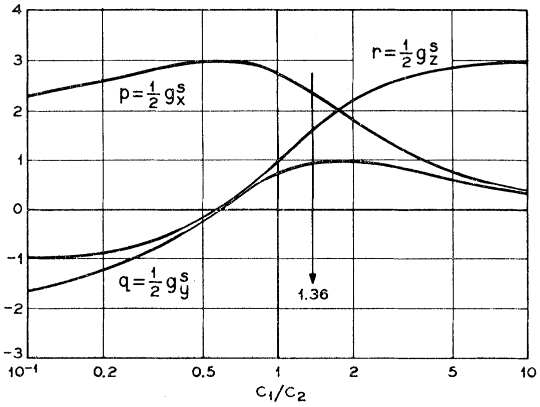

FIG. 2. Theoretical values of spin contribution to the g values of the lowest Kramers doublet as functions of the crystal-field parameters γ and δ [see Eq. (2.7)].

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doublets. As an example we may cite the magnetic susceptibility perpendicular to the c axis for $T > T_N$. This we shall evaluate by molecular field theory and the resulting calculation involves only x and y matrix elements. Writing $C_1 = 1.47 C_2$ allows us to reproduce Kamimura's S_x and S_y ground doublet matrix elements to within about 1%. Also, molecular-field calculations in the absence of magnetic field (or with a field parallel to the c axis) are most accurate if the S_z matrix element is "correctly" reproduced. This is the case when $C_1 = 1.32\, C_2$. In short, the numerical values to be used for γ and δ in any particular theoretical result will be chosen to give the best estimates for those spin-matrix elements which are involved in the calculation.

We are now in a position to write down a Hamiltonian for the entire lattice of cobalt spins. We include exchange interactions (between $S = \frac{3}{2}$ spins) which we assume to be isotropic and to exist between nearest neighbors (same sublattice) and between next nearest neighbors (opposite sublattices). We neglect dipolar interactions since they contribute only $\approx 2\%$ to total anisotropy. Noting (Fig. 1) that the corner cations and the body-center cations have environments which differ by a 90° rotation about the c axis, we write a Hamiltonian for the system in the form

$$\mathcal{H} = \sum_j [\gamma(S_{jy}^2 - S_{jx}^2) + \delta S_{jz}^2] + \sum_k [\gamma(S_{kx}^2 - S_{ky}^2) + \delta S_{kz}^2] + \sum_{nn} J_1(\mathbf{S}_j \cdot \mathbf{S}_{j'} + \mathbf{S}_k \cdot \mathbf{S}_{k'}) + \sum_{nnn} J_2 \mathbf{S}_j \cdot \mathbf{S}_k\,, \quad (2.13)$$

where J_1 and J_2 are the exchange parameters for interactions between nearest and next nearest neighbors, respectively, and where subscripts j and k refer to spins on the "up" and "down" sublattices.

In order to determine the values of J_1 and J_2 which exist in CoF_2 we shall attempt to formulate a spin-wave description of this system. If the crystal-field terms in (2.13) are much larger than the exchange terms, then a good description of the system can be obtained in terms of an effective spin-$\frac{1}{2}$ Hamiltonian. Such a spin-wave description has been given by Kamimura[19] who finds that it is not able to account for experimental results concerning antiferromagnetic resonance. A description of this type neglects completely the existence of the upper doublet states (2.3), (2.4). On the other hand, if the exchange terms in (2.13) dominate, the system can be described in terms of spin deviations from the $S_z = \pm\frac{3}{2}$ states. Unfortunately, rough molecular-field calculations seem to indicate that for CoF_2 the crystal field and exchange terms are of the same order of magnitude, and Nakamura and Taketa[1] suggest that $\langle S_z \rangle$ in the ordered state is of the order 1.2 (we shall later calculate a value 1.06). This would indicate an extremely large deviation from the $S_z = \frac{3}{2}$ state even at $T = 0$°K and make any spin-wave theory (even including spin-wave interactions) which is formulated in terms of deviations from the $\frac{3}{2}$ state very dubious.

In the present paper we shall first treat Eq. (2.13) by molecular field theory to obtain single-ion eigenstates. We shall then introduce spin-wave operators which describe the deviations of the spins from the molecular field state. It seems reasonable to hope that the latter are small and indeed the final numerical results seem to indicate that this is so.

3. MOLECULAR FIELD THEORY

For a molecular-field description of the system we consider a single ion spin S_j and replace all the other spin operators by their average values which, in the ordered state, we write as $\pm\bar{S}$. For a spin on the "up" sublattice we find a Hamiltonian

$$\mathcal{H}_j = -\gamma(S_{jx}^2 - S_{jy}^2) + \delta S_{jz}^2 - \alpha S_{jz}\,, \quad (3.1)$$

where

$$\alpha = (z_2 J_2 - z_1 J_1)\bar{S}\,, \quad (3.2)$$

and where z_1 and z_2 are the numbers of nearest and next nearest neighbors of S_j, respectively. We may obtain eigenvalues and eigenfunctions of (3.1) as follows,

$$E_4 = 5\delta/4 + \alpha/2 + [(\delta+\alpha)^2 + 3\gamma^2]^{1/2}\,, \quad (3.3)$$

$$E_3 = 5\delta/4 - \alpha/2 + [(\delta-\alpha)^2 + 3\gamma^2]^{1/2}\,, \quad (3.4)$$

$$E_2 = 5\delta/4 + \alpha/2 - [(\delta+\alpha)^2 + 3\gamma^2]^{1/2}\,, \quad (3.5)$$

$$E_1 = 5\delta/4 - \alpha/2 - [(\delta-\alpha)^2 + 3\gamma^2]^{1/2}\,, \quad (3.6)$$

$$\psi_4 = d|\tfrac{3}{2}, -\tfrac{3}{2}\rangle - c|\tfrac{3}{2}, \tfrac{1}{2}\rangle\,, \quad (3.7)$$

$$\psi_3 = b|\tfrac{3}{2}, \tfrac{3}{2}\rangle - a|\tfrac{3}{2}, -\tfrac{1}{2}\rangle\,, \quad (3.8)$$

$$\psi_2 = c|\tfrac{3}{2}, -\tfrac{3}{2}\rangle + d|\tfrac{3}{2}, \tfrac{1}{2}\rangle\,, \quad (3.9)$$

$$\psi_1 = a|\tfrac{3}{2}, \tfrac{3}{2}\rangle + b|\tfrac{3}{2}, -\tfrac{1}{2}\rangle\,, \quad (3.10)$$

where

$$\frac{a}{b} = \frac{[(\delta-\alpha)^2 + 3\gamma^2]^{1/2} + \alpha - \delta}{\sqrt{3}\gamma}\,, \quad (3.11)$$

and

$$\frac{c}{d} = \frac{[(\delta+\alpha)^2 + 3\gamma^2]^{1/2} - \alpha - \delta}{\sqrt{3}\gamma}\,. \quad (3.12)$$

Anticipating the numerical results of the paper, we show in Fig. 3 the positions of the energy levels for CoF_2 at very low temperatures.

Near the Néel point, α is very small, and the energy levels may be expanded in powers of α. Omitting unimportant constant terms, we find, to second order in α

$$\begin{aligned} E_4 &= 175 + f\alpha + h\alpha^2\,, \\ E_3 &= 175 - f\alpha + h\alpha^2\,, \\ E_2 &= g\alpha - h\alpha^2\,, \\ E_1 &= -g\alpha - h\alpha^2\,, \end{aligned} \quad (3.13)$$

where

$$f = \tfrac{1}{2} + \delta/A\,, \quad (3.14)$$

$$g = \tfrac{1}{2} - \delta/A\,, \quad (3.15)$$

$$h = 3\gamma^2/2A^3\,, \quad (3.16)$$

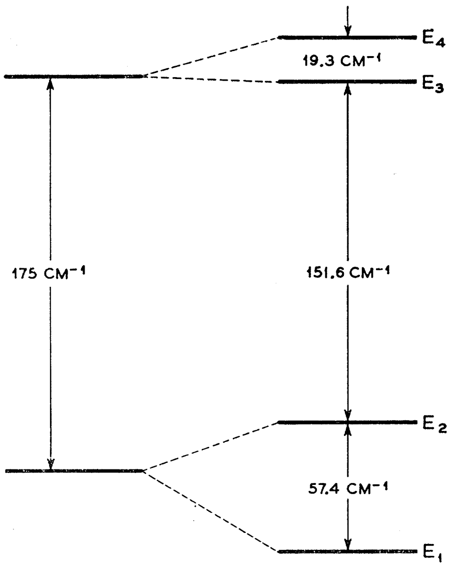

FIG. 3. Molecular-field energy levels of the lowest four states of Co^{++} in CoF_2 at very low temperatures, showing the splitting of the doublet levels by the exchange field.

and

$$A=(\delta^2+3\gamma^2)^{1/2}=87.5\,, \tag{3.17}$$

where we shall measure all energies in units cm^{-1}.

The average value of spin $\bar{S}$ on an "up" sublattice site in the molecular-field approximation follows as

$$\bar{S}=\sum_{i=1}^{4}\frac{\partial E_i}{\partial\alpha}\exp[-E_i/kT]\Big/\sum_{i=1}^{4}\exp[-E_i/kT]\,, \tag{3.18}$$

giving, in the immediate vicinity of T_N, the result

$$\bar{S}=\frac{g^2/kT+2h+[f^2/kT-2h]\exp[-175/kT]}{1+\exp[-175/kT]}\alpha\,, \tag{3.19}$$

correct to first order in α.

For CoF_2 the Néel temperature is about 38°K ($kT_N=26.4$).[20] Using this value for kT_N, the exponential terms in (3.19) are negligible and we find

$$z_2J_2-z_1J_1=[g^2/26.4+2h]^{-1}. \tag{3.20}$$

Using values $\gamma=-48.6$ cm^{-1} and $\delta=-23.6$ cm^{-1}, ($C_1=1.32C_2$) which correctly give Kamimura's g_z^s value, we find

$$f=0.23\,,\quad g=0.77\,,\quad h=0.0053\,, \tag{3.21}$$

from which it follows that $z_2J_2-z_1J_1=30.2$ cm^{-1}.

Such a molecular-field calculation of Néel temperature is at best only semiquantitative, but it does serve to illustrate one important point—that the exchange interaction is indeed of the same order of magnitude as the crystal-field terms so that a neglect of the upper states E_3 and E_4 [the $2h$ term in Eq. (3.20)] produces very sizeable errors indeed.

Molecular field theory would always seem to overestimate transition temperatures[21,22] so that the above estimate for exchange is likely to represent a lower limit. However, no really quantitative work has been done on transition temperatures for systems as complex as the present one, so that we have no indication at this stage as to how low the 30.2 cm^{-1} value may be.

4. SPIN-WAVE THEORY

In this section we shall assume that the actual antiferromagnetic ground state is close enough to the molecular-field ground state E_1 for the former to be described in terms of excitations from the latter keeping only terms up to those quadratic in the operators representing spin deviations. We shall thus attempt a noninteracting spin-wave description which we shall find to be adequate for temperatures up to $\approx 0.4T_N$.

The energy levels of Eqs. (3.3) to (3.6) are functions of $(z_2J_2-z_1J_1)\bar{S}$. We are presently concerned with the energy levels for $T\to 0$ and these may be expressed as functions of exchange energy alone by writing $\bar{S}$ as a function of $z_2J_2-z_1J_1$ through the implicit equation

$$\bar{S}_{T\to 0}=\frac{\partial E_1}{\partial\alpha}=\frac{1}{2}\frac{\delta-\alpha}{[(\delta-\alpha)^2+3\gamma^2]^{1/2}}\,, \tag{4.1}$$

which has the solution shown graphically in Fig. 4. The resulting positions of the single-ion energy levels as functions of exchange are as indicated in Fig. 5. We see that for exchange energies of the expected order of magnitude, E_2-E_1 is several times smaller than either E_3-E_1 or E_4-E_1. We shall make use of this fact to simplify the spin-wave calculations as follows.

When we introduce the spin operators S_x, S_y, S_z, we see that they are capable of exciting a system in state E_1 to any of the other three states. We ought, therefore, to

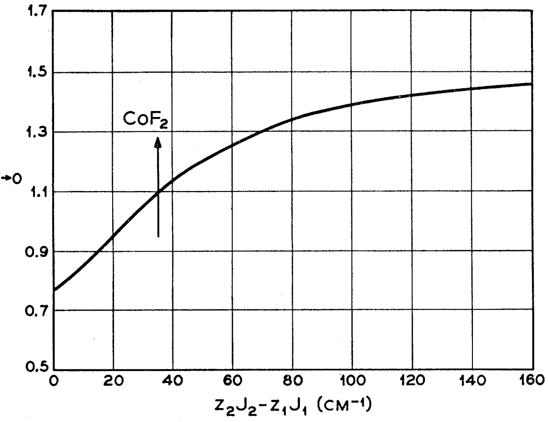

FIG. 4. Molecular-field estimate of the average cobalt spin per ion (in the ground state) as a function of the magnitude of the exchange parameter $z_2J_2-z_1J_1$. The values which we calculate for CoF_2 itself are $z_2J_2-z_1J_1=34.9$ cm^{-1} and $\bar{S}=1.09$.

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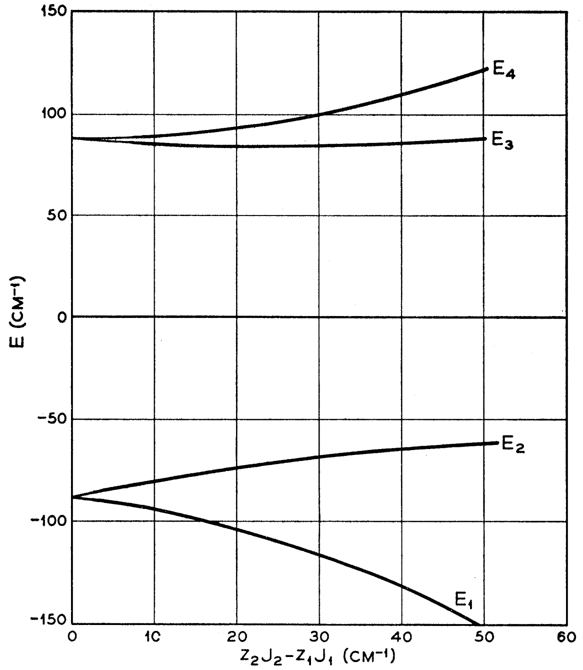

FIG. 5. Energy levels of the four eigenstates of Hamiltonian (3.1) as a function of the exchange parameter $z_2J_2-z_1J_1$, calculated for the limit of very low temperature.

introduce spin-wave operators to represent all of these possible excitations. Because of the above energy-level situation, however, it is fairly safe to assume that for temperatures in the spin-wave region, the excitations to the level E_2 will very largely dominate so that a theory which includes only these excitations will be able to describe the temperature variation of $\bar{S}$ in a satisfactory way. We shall return to a discussion of other spin-wave modes later in this section but, for the present, we shall neglect E_3 and E_4. Note that this approximation is by no means equivalent to that of neglecting the existence of the upper doublet $E_2^{\pm}$ of Eq. (2.3) which was used by Kamimura.[19]

The matrix elements of S_{jx}, S_{jy}, S_{jz} between the levels ψ_1 and ψ_2 [Eqs. (3.9) and (3.10)] may be written

$$S_{jx}=Ps_{jx}\,,\quad S_{jy}=Qs_{jy}\,,\quad S_{jz}=Rs_{jz}+T\,,\qquad(4.2)$$

where s_{jx}, s_{jy}, s_{jz}, are the components of a spin-$\frac{1}{2}$ operator $\mathbf{s}_j$ and where

$$P=\sqrt{3}bc+\sqrt{3}ad+2bd\,,\qquad(4.3)$$

$$Q=\sqrt{3}bc+\sqrt{3}ad-2bd\,,\qquad(4.4)$$

$$2R=3a^2-b^2+3c^2-d^2\,,\qquad(4.5)$$

$$4T=3a^2-b^2-3c^2+d^2\,,\qquad(4.6)$$

with a, b, c, d, from Eqs. (3.11) and (3.12) and with wave functions normalized to unity so that

$$a^2+b^2=1\,,\quad c^2+d^2=1\,.\qquad(4.7)$$

We take the subscript j to indicate spins on the "up" sublattice so that the molecular-field state has s_{jz} in eigenstate $+\frac{1}{2}$.

In an exactly similar manner we find that the "down" spins have matrix elements between their lowest two molecular-field states which may be written in terms of a spin-$\frac{1}{2}$ operator $\mathbf{s}_k$ as

$$S_{kx}=Qs_{kx}\,,\quad S_{ky}=Ps_{ky}\,,\quad S_{kz}=Rs_{kz}-T\,,\qquad(4.8)$$

where the molecular-field state has eigenvalue $s_{kz}=-\frac{1}{2}$.

We may now express the exchange Hamiltonian, given by

$$\mathcal{H}_{\text{ex}}=\sum_{nn}J_1(S_j\cdot S_{j'}+S_k\cdot S_{k'})+\sum_{nnn}J_2S_j\cdot S_k\,,\qquad(4.9)$$

in terms of the above spin-$\frac{1}{2}$ operators. In this way we represent the system by the 'effective' spin-$\frac{1}{2}$ Hamiltonian

$$\begin{aligned}\mathcal{H}_{\text{ex}}=&\sum_{nn}J_1'[P^2s_{jx}s_{j'x}+Q^2s_{jy}s_{j'y}+(Rs_{jz}+T)(Rs_{j'z}+T)]\\&+\sum_{nn}J_1'[Q^2s_{kx}s_{k'x}+P^2s_{ky}s_{k'y}+(Rs_{kz}-T)\\&\times(Rs_{k'z}-T)]+\sum_{nnn}J_2'[PQ(s_{jx}s_{kx}+s_{jy}s_{ky})\\&+(Rs_{jz}+T)(Rs_{kz}-T)]\,,\end{aligned}\qquad(4.10)$$

where the exchange interactions J_1' and J_2' are chosen so that the exchange energy difference between the molecular-field states $s_{jz}=+\frac{1}{2}$ and $s_{jz}=-\frac{1}{2}$ is equal to E_2-E_1 [Eqs. (3.5), (3.6)]. This condition is

$$(z_2J_2'-z_1J_1')R(T+\tfrac{1}{2}R)=E_2-E_1\,,\qquad(4.11)$$

and the primed parameters differ slightly from the unprimed ones (see Fig. 6) because the spin-wave

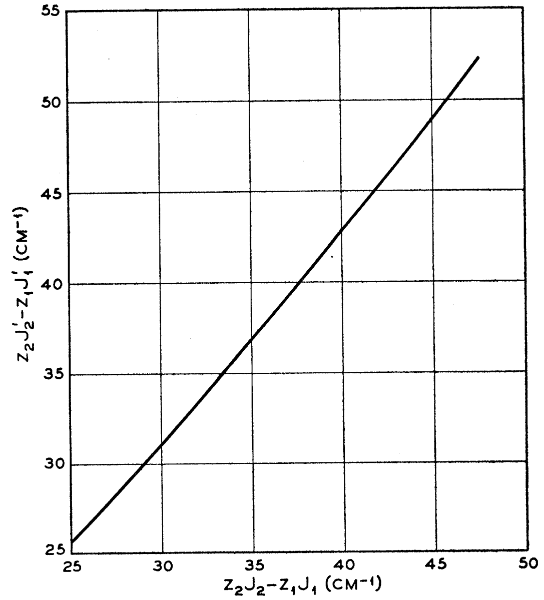

FIG. 6. The relationship between the primed and unprimed exchange parameters of Hamiltonians (2.13) and (4.10) which gives the same energy separation between the lowest two molecular-field eigenvalues in both cases.

Hamiltonian neglects the states E_3 and E_4. We assume that $J_1/J_2=J_1'/J_2'$.

The spin-wave creation and annihilation operators of Holstein and Primakoff[23] may now be introduced into the Hamiltonian (4.10). Following Kubo[24] we define Bose operators for the "up" and the "down" spins by the equations

$$s_{jz}=s-a_j^*a_j,\quad s_j^+=(2s)^{1/2}a_j,\quad s_j^-=(2s)^{1/2}a_j^*,\tag{4.12}$$

$$s_{kz}=-s+b_k^*b_k,\quad s_k^+=(2s)^{1/2}b_k^*,\quad s_k^-=(2s)^{1/2}b_k,\tag{4.13}$$

where $s=\frac{1}{2}$, and where $s^\pm=s_x\pm is_y$.

Using the canonical transformation

$$\sqrt{2}a_j=Q_j+iP_j,\quad \sqrt{2}a_j^*=Q_j-iP_j,\tag{4.14}$$

$$\sqrt{2}b_k=R_k+iS_k,\quad \sqrt{2}b_k^*=R_k-iS_k,\tag{4.15}$$

we introduce spin-wave variables $P_{\mathbf{K}}$, $Q_{\mathbf{K}}$, $R_{\mathbf{K}}$, $S_{\mathbf{K}}$, in the form

$$\begin{aligned}P_{\mathbf{K}}&=(2/N)^{1/2}\sum_j P_je^{i\mathbf{K}\cdot\mathbf{j}},\\ Q_{\mathbf{K}}&=(2/N)^{1/2}\sum_j Q_je^{-i\mathbf{K}\cdot\mathbf{j}},\end{aligned}\tag{4.16}$$

$$\begin{aligned}S_{\mathbf{K}}&=(2/N)^{1/2}\sum_k S_ke^{-i\mathbf{K}\cdot\mathbf{k}},\\ R_{\mathbf{K}}&=(2/N)^{1/2}\sum_k R_ke^{i\mathbf{K}\cdot\mathbf{k}},\end{aligned}\tag{4.17}$$

where $\mathbf{K}$ is a reciprocal lattice vector which takes values determined by periodic boundary conditions (running over $N/2$ points in the first Brillouin zone of the reciprocal sublattice), and where N is the number of spins in the entire lattice. The resulting Hamiltonian is

$$\begin{aligned}\mathcal{H}=&-\tfrac{1}{2}Nx[s(s+1)R^2+(2s+1)RT+T^2]\\&+\tfrac{1}{2}s\sum_{\mathbf{K}}[a_{\mathbf{K}}(Q_{\mathbf{K}}^2+S_{\mathbf{K}}^2)+b_{\mathbf{K}}(P_{\mathbf{K}}^2+R_{\mathbf{K}}^2)\\&+2c_{\mathbf{K}}(Q_{\mathbf{K}}R_{\mathbf{K}}-P_{\mathbf{K}}S_{\mathbf{K}})],\end{aligned}\tag{4.18}$$

where

$$a_{\mathbf{K}}=Rx(R+T/s)+J_1'P^2\sum_{nn}e^{i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}_0)},\tag{4.19}$$

$$b_{\mathbf{K}}=Rx(R+T/s)+J_1'Q^2\sum_{nn}e^{i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}_0)},\tag{4.20}$$

$$c_{\mathbf{K}}=J_2'PQ\sum_{nnn}e^{i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}_0)},\tag{4.21}$$

$$x=z_2J_2'-z_1J_1',\tag{4.22}$$

and where $\sum_{nn}(\sum_{nnn})$ means the sum over all nearest neighbors (next nearest neighbors) $\mathbf{r}$ of $\mathbf{r}_0$.

This Hamiltonian may be written in diagonal form in terms of the canonically conjugate variables $q_{1\mathbf{K}}$, $p_{1\mathbf{K}}$, and $q_{2\mathbf{K}}$, $p_{2\mathbf{K}}$ which are defined by

$$q_{1\mathbf{K}}=Q_{\mathbf{K}}\cos\theta+R_{\mathbf{K}}\sin\theta,\tag{4.23}$$

$$p_{1\mathbf{K}}=P_{\mathbf{K}}\cos\theta+S_{\mathbf{K}}\sin\theta,\tag{4.24}$$

$$q_{2\mathbf{K}}=R_{\mathbf{K}}\cos\theta-Q_{\mathbf{K}}\sin\theta,\tag{4.25}$$

$$p_{2\mathbf{K}}=S_{\mathbf{K}}\cos\theta-P_{\mathbf{K}}\sin\theta,\tag{4.26}$$

where $\tan(2\theta)=2c_{\mathbf{K}}/(a_{\mathbf{K}}-b_{\mathbf{K}})$. We obtain

$$\begin{aligned}\mathcal{H}=&-\tfrac{1}{2}Nx[s(s+1)R^2+(2s+1)RT+T^2]\\&+\tfrac{1}{2}s\sum_{\mathbf{K}}[d_{\mathbf{K}}(q_{1\mathbf{K}}^2+p_{2\mathbf{K}}^2)+e_{\mathbf{K}}(q_{2\mathbf{K}}^2+p_{1\mathbf{K}}^2)],\end{aligned}\tag{4.27}$$

where

$$d_{\mathbf{K}}=a_{\mathbf{K}}\cos^2\theta+b_{\mathbf{K}}\sin^2\theta+2c_{\mathbf{K}}\sin\theta\cos\theta,\tag{4.28}$$

$$e_{\mathbf{K}}=a_{\mathbf{K}}\sin^2\theta+b_{\mathbf{K}}\cos^2\theta-2c_{\mathbf{K}}\sin\theta\cos\theta,\tag{4.29}$$

and we may thus write eigenvalues

$$\begin{aligned}E_{n_1n_2}=&-\tfrac{1}{2}Nx[s(s+1)R^2+(2s+1)RT+T^2]\\&+s\sum_{\mathbf{K}}(n_{1\mathbf{K}}+n_{2\mathbf{K}}+1)(a_{\mathbf{K}}b_{\mathbf{K}}-c_{\mathbf{K}}^2)^{1/2},\end{aligned}\tag{4.30}$$

where $n_{1\mathbf{K}}$ and $n_{2\mathbf{K}}$ are positive integers denoting the number of spin waves present in the eigenstate $E_{n_1n_2}$ with wave vector $\mathbf{K}$.

Since the average values of kinetic and potential energies are equal for a simple harmonic oscillator, we have

$$d_{\mathbf{K}}\langle q_{1\mathbf{K}}^2\rangle=e_{\mathbf{K}}\langle p_{1\mathbf{K}}^2\rangle=\langle n_{1\mathbf{K}}+\tfrac{1}{2}\rangle(a_{\mathbf{K}}b_{\mathbf{K}}-c_{\mathbf{K}}^2)^{1/2},\tag{4.31}$$

$$d_{\mathbf{K}}\langle p_{2\mathbf{K}}^2\rangle=e_{\mathbf{K}}\langle q_{2\mathbf{K}}^2\rangle=\langle n_{2\mathbf{K}}+\tfrac{1}{2}\rangle(a_{\mathbf{K}}b_{\mathbf{K}}-c_{\mathbf{K}}^2)^{1/2},\tag{4.32}$$

where the pointed brackets indicate ensemble averages. In order to calculate the value of sublattice spin $\bar{S}$ in the spin-wave region we consider the "up" sublattice for which we have, from Eq. (4.2),

$$\bar{S}=R\bar{s}+T,\tag{4.33}$$

where

$$\bar{s}=\tfrac{1}{2}-\langle a_j^*a_j\rangle.\tag{4.34}$$

Using the same set of canonical transformations which were used to diagonalize the Hamiltonian we find

$$\begin{aligned}\bar{S}=T+R-(R/N)\Big\langle\sum_{\mathbf{K}}[&(q_{1\mathbf{K}}^2+p_{1\mathbf{K}}^2)\cos^2\theta\\&+(q_{2\mathbf{K}}^2+p_{2\mathbf{K}}^2)\sin^2\theta]\Big\rangle,\end{aligned}\tag{4.35}$$

where we have used the relations $\langle q_{1\mathbf{K}}q_{2\mathbf{K}}\rangle=0$ and $\langle p_{1\mathbf{K}}p_{2\mathbf{K}}\rangle=0$ which are valid because the associated oscillators are independent. We now insert the correct value for θ and make use of Eqs. (4.31) and (4.32) when we obtain

$$\bar{S}=T+R-(R/N)\sum_{\mathbf{K}}\frac{a_{\mathbf{K}}+b_{\mathbf{K}}}{(a_{\mathbf{K}}b_{\mathbf{K}}-c_{\mathbf{K}}^2)^{1/2}}\langle n_{\mathbf{K}}+\tfrac{1}{2}\rangle,\tag{4.36}$$

where the ensemble average $\langle n_{\mathbf{K}}+\frac{1}{2}\rangle$ at temperature T is readily evaluated as

$$\langle n_{\mathbf{K}}+\tfrac{1}{2}\rangle=\tfrac{1}{2}\coth[s(a_{\mathbf{K}}b_{\mathbf{K}}-c_{\mathbf{K}}^2)^{1/2}/2kT].\tag{4.37}$$

The final spin-wave expression for sublattice spin is thus

$$\bar{S}=T+R-\tfrac{1}{4}R\Big\langle\frac{(a_{\mathbf{K}}+b_{\mathbf{K}})}{(a_{\mathbf{K}}b_{\mathbf{K}}-c_{\mathbf{K}}^2)^{1/2}}\times\coth\Big[\frac{(a_{\mathbf{K}}b_{\mathbf{K}}-c_{\mathbf{K}}^2)^{1/2}}{4kT}\Big]\Big\rangle_{\mathbf{K}},\tag{4.38}$$

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

[24] R. Kubo, Phys. Rev. **87**, 568 (1952).

where $\langle\cdots\rangle_K$ is the average value for **K** running over its $N/2$ allowed values in the first Brillouin zone of the reciprocal sublattice. We have calculated the numerical results for $\bar{S}$ as a function of temperature using (4.38) and evaluating the Brillouin-zone averages by computer. Several different values for J_1' and J_2' were chosen and the results are shown graphically in Figs. 7 and 8 where spin deviation from the $T=0$ state is plotted against temperature and compared with the experimental results of Jaccarino.[8] These graphs have been labeled in terms of the unprimed exchange parameters by use of Fig. 6. We see that a good fit of theory with experiment may be obtained for temperatures up to ≈ 15°K (with $z_2J_2-z_1J_1=35$ cm^{-1}, $J_1/J_2=0$, for example) which is about 40% of the Néel temperature, but it is not possible to determine J_1 and J_2 separately by using this data alone. We shall accomplish this below by including the antiferromagnetic resonance data together with the spin-deviation results.

For temperatures above $2T_N/5$ the theoretical spin deviations are smaller than the measured ones, the discrepancy increasing with rising temperature. For the present system, this is due not only to the usual cause, which is the neglect of spin-wave interaction terms, but also to the fact that the parameters P, Q, R, T, [which are employed in the construction of the spin Hamiltonian (4.10)] are calculated by assuming that $\bar{S}$ has its molecular-field ground-state value. This approximation will become poorer as temperature increases and will break down completely for temperatures approaching the Néel point.

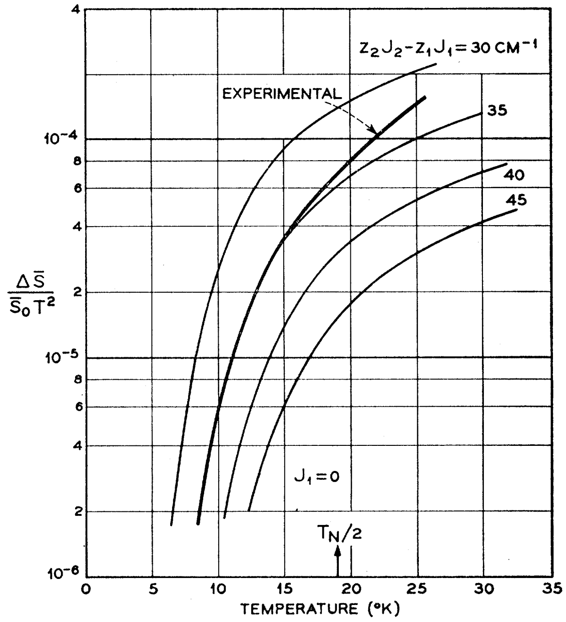

FIG. 7. Theoretical spin-wave estimates of the deviation of spin $\Delta\bar{S}$ from its value $\bar{S}_0$ at the absolute zero of temperature plotted as a function of temperature. These curves are all evaluated for the case when $J_1=0$. Also shown are the experimental results from nuclear resonance experiments.[8]

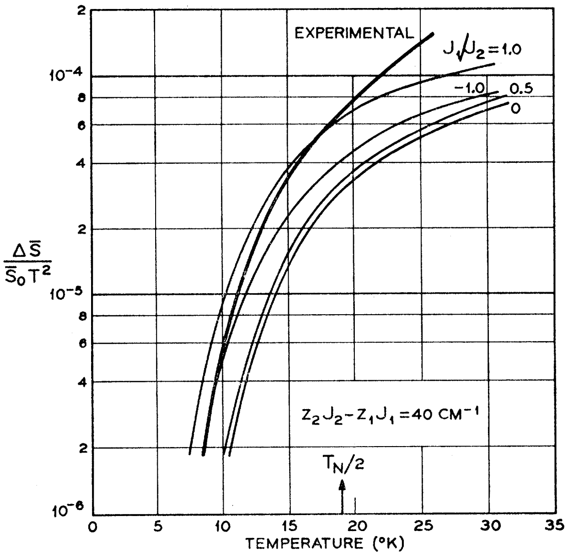

FIG. 8. Theoretical estimates of spin deviation $\Delta\bar{S}$ from the zero temperature value $\bar{S}_0$ as a function of temperature T. These curves are all calculated for the same value of "molecular field" ($z_2J_2-z_1J_1=40$ cm^{-1}) and show the effects which may be obtained by varying the ratio of the exchange parameters while keeping the effective field fixed.

It is also of interest to note that although the spin deviation is mainly dependent on the "molecular field" parameter $z_2J_2-z_1J_1$, it is also sensitive to variations of J_1/J_2 keeping the former parameter fixed (Fig. 8). This is particularly so when the system approaches an instability (e.g., the point where a different spin pattern becomes more stable). The case $J_1/J_2=1$ (Fig. 8) is such an example, the ratio being close to that for which a screw-type spin arrangement[25] becomes the stable ordering. The actual "critical ratio" is that above which some of the spin-wave frequencies $(a_Kb_K-c_K^2)^{1/2}$ take imaginary values. For the case $z_2J_2-z_1J_1=40$ cm^{-1} which is shown in Fig. 8, this ratio is $J_1/J_2=1.44$.

In order to determine the exchange interactions separately we consider the antiferromagnetic resonance data. Richards[7] reports two resonances, a weak one at 28.5 cm^{-1} and a much stronger one at 36 cm^{-1}. In the presence of a magnetic field along the c axis, the resonances split with g factors 1.18 and 2.80, respectively. From the theory of the present section we find only a single resonance frequency (associated with the $\mathbf{K}=0$ spin-wave modes) which is given by

$$\omega_0=\tfrac{1}{2}(a_0b_0-c_0^2)^{1/2}, \tag{4.39}$$

where

$$a_0=Rx(R+2T)+P^2z_1J_1', \tag{4.40}$$

$$b_0=Rx(R+2T)+Q^2z_1J_1', \tag{4.41}$$

$$c_0=PQz_2J_2'. \tag{4.42}$$

A consistent solution for spin deviation and resonance

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[25] A. Yoshimori, J. Phys. Soc. (Japan) 14, 807 (1959).

frequency can only be found if ω_0 is identified with the 36 cm^{-1} resonance. We shall confirm this choice by a calculation of the associated resonance g factor, the theory of which will be given in the next section. Using this frequency we find agreement of theory and experiment if $z_2J_2-z_1J_1=34.9$ cm^{-1} ($x=36.8$ cm^{-1}) and $J_1/J_2\approx -0.1$. Putting $z_2=8$ and $z_1=2$ we obtain values $J_1=-0.5$ cm^{-1} and $J_2=4.25$ cm^{-1}. Because of the approximations contained in the theory, not too much weight should be attached to the exact numerical result for J_1. It does seem, however, that J_1 is certainly very small compared to J_2 and is probably ferromagnetic in sign. Using the above values for exchange we find that:

(a) The single ion molecular-field energy levels are as shown in Fig. 3.

(b) The associated wave functions are given by Eqs. (3.7) to (3.10) with parameters $a=0.89$, $b=0.45$, $c=0.64$, $d=0.77$.

(c) The parameters P, Q, R, T, defined by Eqs. (4.3) to (4.6), have values $P=0.99$, $Q=2.38$, $R=1.42$, $T=0.38$.

(d) The molecular-field estimate of spin $\bar{S}$ in the ground state is 1.09.

(e) The spin-wave estimate for $\bar{S}$ differs by 2.9% from the molecular-field value being very close to 1.06.

The second (weaker) resonance would seem to be only one of several other possible antiferromagnetic resonance frequencies. In the present theory, for reasons stated earlier, we have included only those spin operators which describe excitations between states E_1 and E_2 (Fig. 3). Since E_1 is not the correct ground state even at the absolute zero of temperature (because of the presence of zero-point spin-waves), a more accurate treatment of the problem should include operators representing excitations not only between the ground molecular-field state and E_3 and E_4, but also between E_2 and E_3; E_2 and E_4; and E_3 and E_4. Spin waves connected with all six sets of operators may possibly all be present even at absolute zero, and there could thus be as many as six antiferromagnetic resonance modes, three strong ones involving excitations from E_1, and three weaker ones. The only one of these which is likely to be as small as 28.5 cm^{-1} is that associated with the levels E_3 and E_4. Supporting this conjecture is the fact that E_4-E_3 varies with magnetic field parallel to z less than half as fast as does E_2-E_1. We thus expect a much smaller resonance g factor for the 28.5 cm^{-1} mode than for the 36 cm^{-1} one, which agrees qualitatively with observations.[7]

5. MAGNETIC SUSCEPTIBILITY PARALLEL TO THE C AXIS

In this section we introduce an external magnetic field H parallel to the c axis of the lattice which is the direction of spin alignment in the antiferromagnetic state. We include the effect of this magnetic field by adding to the Hamiltonian (2.13) a term of the form $-g_z\mu_BH\sum_j S_{jz}$, where μ_B is the Bohr magneton and where g_z is the Landé g factor for the field parallel to z. We neglect terms containing higher powers of H since even the H^2 term[26] which contributes to the zero-field susceptibilities would seem to modify the latter by only 1 or 2% in the temperature range of interest. The value of g_z may be calculated from the analysis of Kamimura and Tanabe[18] (as also may the g_x and g_y values for use in the following section) so that the problem is now completely determined. With no "adjustables" remaining, we may now calculate the magnetic susceptibilities and compare the results with experiment.[6] We shall, for simplicity, assume that the effects of any intrasublattice exchange are negligible and write $z_2J_2=35$ cm^{-1}, $J_1=0$.

(a) Temperatures Above the Néel Point

Using the molecular-field approximation we write the Hamiltonian for a single spin S_j in the form (3.1), but where now

$$\alpha=\alpha_H=g_z\mu_BH-\bar{S}(z_1J_1+z_2J_2)=g_z\mu_BH_{\text{eff}}, \quad (5.1)$$

where $\bar{S}$ is the average value of spin per site and H_{eff} is the effective magnetic field acting on S_j. Since α_H is very small compared to γ or δ (we are concerned primarily with the limit $\alpha_H\rightarrow 0$) we may write the eigenvalues in the form (3.13). Kamimura and Tanabe[18] find that the lowest doublet splits as $\pm\frac{1}{2}g_z'\mu_BH_{\text{eff}}$ where $g_z'=4.07$. Using (3.13) we have, therefore,

$$gg_z=2.035, \quad (5.2)$$

where $g=0.77$ [Eq. (3.21)]. It follows that $g_z=2.64$. The average spin per site is given by (3.19) from which, by substituting for α from (5.1), we obtain the parallel susceptibility $\chi_{\parallel}$ in the form

$$\chi_{\parallel}=\frac{Ng_z^2\mu_B^2F(T)}{1+(z_1J_1+z_2J_2)F(T)}, \quad (5.3)$$

where

$$F(T)=\frac{g^2/kT+2h+[f^2/kT-2h]\exp[-175/kT]}{1+\exp[-175/kT]}, \quad (5.4)$$

where f, g, h, take the values given in (3.21), and kT is measured in cm^{-1} energy units.

The above susceptibility is plotted as a function of temperature in Fig. 9. Except for the expected deviation in the vicinity of T_N (due to the inability of molecular field theory to describe the system adequately in this region—see, for example, Li[27]) the agreement with experiment is excellent.

(b) Temperatures Approaching Absolute Zero

For temperatures below T_N we must distinguish between spins on the two sublattices. In the presence

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[26] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

[27] Y. Y. Li, Phys. Rev. **84**, 721 (1951).

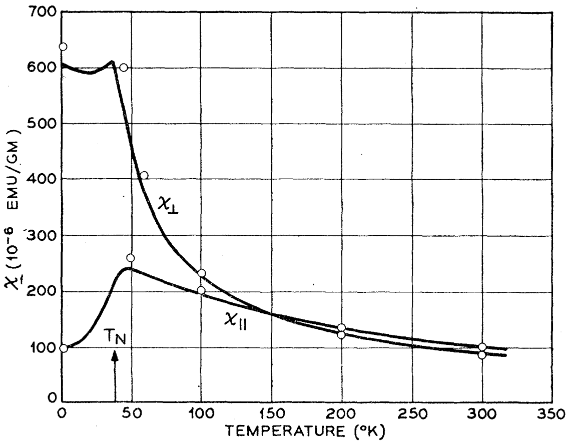

FIG. 9. Molecular-field estimates of parallel and perpendicular magnetic susceptibilities (open circles) in the temperature range zero to 300°K are compared with the experimental curves obtained by Foner.[6]

of the magnetic field H parallel to the c axis, we write the average "up" spin as $\bar{S}+\Delta\bar{S}$ and the average "down" spin as $-\bar{S}+\Delta\bar{S}$.

In the molecular-field approximation, the Hamiltonian for spin S_j on the "up" sublattice may be written in the form (3.1), but where now

$$\alpha=\alpha_H=g_z\mu_B H+(\bar{S}-\Delta\bar{S})z_2J_2-(\bar{S}+\Delta\bar{S})z_1J_1. \quad (5.5)$$

For temperatures close to absolute zero, the average spin on an "up" sublattice is given, to a good approximation, by (4.1), which, on writing

$$\alpha_H=(z_2J_2-z_1J_1)\bar{S}+\epsilon=\alpha_0+\epsilon, \quad (5.6)$$

where

$$\epsilon=g_z\mu_B H-(z_1J_1+z_2J_2)\Delta\bar{S}, \quad (5.7)$$

may be expanded in powers of ϵ, and gives, to first order,

$$\bar{S}+\Delta\bar{S}=\bar{S}+\frac{3\gamma^2\epsilon}{[(\delta-\alpha_0)^2+3\gamma^2]^{3/2}}. \quad (5.8)$$

Using (5.7) it follows that the magnetic susceptibility at zero temperature is

$$\chi_0=\frac{3Ng_z^2\mu_B^2\gamma^2}{[(\delta-\alpha_0)^2+3\gamma^2]^{3/2}+3\gamma^2(z_1J_1+z_2J_2)}, \quad (5.9)$$

and, putting $g_z=2.64$, $\gamma=-48.6$ cm^{-1}, and $\delta=-23.6$ cm^{-1}, this has a numerical value of 96 10^{-6} emu/g which (see Fig. 9) is again in very good agreement with experiment. We may also evaluate $(z_1J_1+z_2J_2)\Delta\bar{S}$, which will be required in the following subsection, and we find it to be equal to 0.18 $g_z\mu_B H$. It follows that $\epsilon=0.82\ g_z\mu_B H$.

(c) Splitting Factor for Antiferromagnetic Resonance

The molecular-field representation of the system at low temperatures is given by (3.1), where α is defined by (5.5). The eigenvalues of (3.1) are given in Eqs. (3.3) to (3.6) and we shall be interested in the lowest two states E_1 and E_2. Writing α_H as in (5.6), we expand in powers of ϵ to obtain

$$E_2^H=E_2^0+\left[\frac{1}{2}-\frac{\delta+(z_2J_2-z_1J_1)\bar{S}}{[(\delta+\alpha_0)^2+3\gamma^2]^{1/2}}\right]\epsilon+\cdots, \quad (5.10)$$

and

$$E_1^H=E_1^0-\left[\frac{1}{2}-\frac{\delta-(z_2J_2-z_1J_1)\bar{S}}{[(\delta-\alpha_0)^2+3\gamma^2]^{1/2}}\right]\epsilon+\cdots, \quad (5.11)$$

where E_1^0 and E_2^0 are the energy levels in the absence of a field. Using $z_2J_2=35$ cm^{-1}, $J_1=0$, we may evaluate the coefficients of ϵ in (5.10) and (5.11) and we find them to be 0.33 and -1.09, respectively. In the presence of a magnetic field the energy separation of E_2^H and E_1^H varies therefore as 1.42 ϵ.

In the spin Hamiltonian (4.10) we can introduce the effect of the magnetic field H by adding terms

$$-g_z''\mu_B H\left[\sum_j(Rs_{jz}+T)+\sum_k(Rs_{kz}-T)\right]. \quad (5.12)$$

It follows that g_z'' must satisfy the equation

$$g_z''R=1.42\epsilon/\mu_B H. \quad (5.13)$$

This may be simplified by using the result $\epsilon=0.82$ $g_z\mu_B H$ to give $g_z''R=3.07$.

Carrying out the spin-wave calculation with magnetic-field terms present, we obtain for the antiferromagnetic resonance frequency

$$\omega_H=\omega_0\pm g_z''R\mu_B H\left[\frac{(a_0+b_0)^2-4c_0^2}{4(a_0b_0-c_0^2)}\right]^{1/2}, \quad (5.14)$$

where ω_0, a_0, b_0, and c_0 are given in Eqs. (4.39) to (4.42). For the case $J_1=0$, the square root factor is unity and the result simplifies to

$$\omega_H=\omega_0\pm g_R\mu_B H, \quad (5.15)$$

where the resonance splitting factor $g_R=g_z''R=3.07$ which is to be compared with the experimental value 2.80.

6. MAGNETIC SUSCEPTIBILITY PERPENDICULAR TO THE C AXIS

(a) Temperatures Above the Néel Point

Let us introduce an external magnetic field H parallel to the x axis. In the molecular-field approximation we may write the Hamiltonian for an arbitrary spin S_j in the form

$$\mathcal{H}_j=\gamma_i(S_{jx}^2-S_{jy}^2)+\delta S_{jz}^2-\alpha_i S_{jx}, \quad (i=1,2) \quad (6.1)$$

where we have introduced the suffix i to distinguish between the two different types of cation sites (differing from each other by a 90° rotation about the c axis) and where we define $\gamma_1=+\gamma$, $\gamma_2=-\gamma$, and

$$\alpha_1=g_x\mu_BH-z_2J_2\bar{S}_2-z_1J_1\bar{S}_1, \tag{6.2}$$

$$\alpha_2=g_y\mu_BH-z_2J_2\bar{S}_1-z_1J_1\bar{S}_2, \tag{6.3}$$

where $\bar{S}_1$ and $\bar{S}_2$ are the average values of spin on the type-1 and type-2 sites, respectively.

The Hamiltonian (6.1) has eigenvalues which may be expanded as power series in α_i in the form

$$\begin{aligned} E_4&=5\delta/4+A+f_i\alpha_i+h_i\alpha_i^2+\cdots, \\ E_3&=5\delta/4+A-f_i\alpha_i+h_i\alpha_i^2+\cdots, \\ E_2&=5\delta/4-A+g_i\alpha_i-h_i\alpha_i^2+\cdots, \\ E_1&=5\delta/4-A-g_i\alpha_i-h_i\alpha_i^2+\cdots, \end{aligned} \tag{6.4}$$

where

$$f_i=\tfrac{1}{2}+(3\gamma_i-\delta)/2A, \tag{6.5}$$

$$g_i=\tfrac{1}{2}-(3\gamma_i-\delta)/2A, \tag{6.6}$$

$$h_i=3(\delta+\gamma_i)^2/8A^3, \tag{6.7}$$

and

$$A=(\delta^2+3\gamma^2)^{1/2}=87.5\text{ cm}^{-1}. \tag{6.8}$$

The values to be used for δ and γ have been discussed in Sec. 2 and are those which will allow for the best estimate of the matrix elements of S_x and S_y in the ground states of the unperturbed system. These are obtained by putting $C_1=1.47C_2$ in Eq. (2.7). Using (6.8) we find values $\gamma=-47.0$ cm^{-1} and $\delta=-32.0$ cm^{-1}.

We may now write equations for the average values of spin on the two types of site by employing equations of type (3.18) and using energy levels (6.4). We find

$$\bar{S}_i=F_i(T)\alpha_i, \quad (i=1,2) \tag{6.9}$$

where

$$F_i(T)=\frac{g_i^2/kT+2h_i+[f_i^2/kT-2h_i]\exp(-175/kT)}{1+\exp(-175/kT)}, \tag{6.10}$$

and where energies kT are measured in units of cm^{-1}.

Solving the Eqs. (6.9) for $\bar{S}_1$ and $\bar{S}_2$ using (6.2) and (6.3), the perpendicular susceptibility follows as

$$\chi_\perp=\frac{N\mu_B^2[g_x^2F_1+g_y^2F_2+(g_x^2+g_y^2)F_1F_2z_1J_1-2g_xg_yF_1F_2z_2J_2]}{2[1+(F_1+F_2)z_1J_1+F_1F_2(z_1^2J_1^2-z_2^2J_2^2)]}. \tag{6.11}$$

Before a numerical calculation can be completed we require values for g_x and g_y. These follow from the calculations of Kamimura and Tanabe[18] who report that the lowest states E_1 and E_2 of (6.4) split in a magnetic field as $\pm\frac{1}{2}g_i'\mu_BH_{\text{eff}}$ where $g_1'=6.18$, $g_2'=2.03$, and $\alpha_1=g_x\mu_BH_{\text{eff}}$, $\alpha_2=g_y\mu_BH_{\text{eff}}$. It follows that

$$g_1g_x=3.09, \quad g_2g_y=1.015, \tag{6.12}$$

from which, using (6.6), we find $g_x=2.75$, and $g_y=2.08$. We may now calculate $\chi_\perp$ numerically as a function of temperature (using $z_2J_2=35$ cm^{-1}, $J_1=0$) and the result is shown in Fig. 9. The agreement between theory and experiment is again excellent except in the immediate vicinity of the Néel temperature.

(b) Temperatures Approaching Absolute Zero

In the absence of a magnetic field the energy levels of a single spin "up" system S_j are given, in the ordered state, by Eqs. (3.3) to (3.6). In order to calculate the perpendicular susceptibility we shall introduce a magnetic field H in the x direction and perturb the system with the Hamiltonian

$$\mathcal{H}=-\alpha_1S_{jx}, \tag{6.13}$$

where

$$\alpha_1=g_x\mu_BH-z_1J_1\bar{S}_1-z_2J_2\bar{S}_2, \tag{6.14}$$

and where $\bar{S}_1$ and $\bar{S}_2$ are the average x components of spin on the "up" and "down" sites, respectively. The energy of the perturbed ground level is

$$E_1^H=E_1+\frac{[\sqrt{3}(ad+bc)+2bd]^2\alpha_1^2}{4(E_1-E_2)}+\frac{[\sqrt{3}(bd-ac)-2bc]^2\alpha_1^2}{4(E_1-E_4)}, \tag{6.15}$$

where E_1, E_2, E_4, a, b, c, d, are given by Eqs. (3.3) to (3.6), (3.11), (3.12), and (4.7).

For a spin on the "down" sublattice we obtain a similar result but where $a\to -a$, $c\to -c$, and $\alpha_1\to\alpha_2$ where

$$\alpha_2=g_y\mu_BH-z_1J_1\bar{S}_2-z_2J_2\bar{S}_1. \tag{6.16}$$

Thus, we may write for a spin on the "up" sublattice

$$E_1^H=E_1-\tfrac{1}{2}f_1\alpha_1^2, \tag{6.17}$$

and, for a spin on the "down" sublattice

$$E_1^H=E_1-\tfrac{1}{2}f_2\alpha_2^2, \tag{6.18}$$

where f_1 and f_2 are numerical factors which may be evaluated once we have chosen values for γ and δ.

It follows from the above equations that, for temperatures close to absolute zero,

$$\bar{S}_1=f_1\alpha_1, \quad \bar{S}_2=f_2\alpha_2. \tag{6.19}$$

Solving for $\bar{S}_1$ and $\bar{S}_2$ explicitly, the susceptibility follows immediately as $N\mu_B(g_x\bar{S}_1+g_y\bar{S}_2)/2H$ and is given by

Eq. (6.11) if we replace F_1, F_2, by f_1, f_2. For the present case, where we put $J_1=0$, this reduces to

$$(\chi_\perp)_{T=0}=N\mu_B^2[g_x^2f_1+g_y^2f_2-2g_xg_yf_1f_2z_2J_2]/2[1-f_1f_2z_2^2J_2^2]. \quad (6.20)$$

As pointed out in Sec. 2, it is not possible to choose values of γ and δ which will enable the effective spin-$\frac{3}{2}$ Hamiltonian which we use throughout this work to give exactly the correct matrix elements for all three spin components in the ground states of the "zero exchange" system. The calculation of the low-temperature perpendicular susceptibility does involve S_x, S_y, and S_z and the best we can do is to choose γ and δ as in (2.12) when errors of the order 4% are introduced. In this way we find values $f_1=0.0480$, $f_2=0.0085$, and, using the values for g_x and g_y obtained in the preceding subsection, we calculate the zero-temperature perpendicular susceptibility equal to 637 10^{-6} emu/g which is about 5% larger than the experimental value (Fig. 9).

7. NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance of Co^{59} in CoF$_2$ has been observed by Jaccarino[9] who reports a resonance frequency in zero external magnetic field of 180.4 Mc/sec for temperatures close to absolute zero. In the absence of an external magnetic field, we may write a nuclear Hamiltonian for the system in the form

$$\mathcal{H}=A_z^{59}\bar{S}I_z+\gamma^{59}\hbar H_DI_z, \quad (7.1)$$

where the first term is of standard form[17] (A_z^{59} being the magnetic hyperfine interaction constant) and represents the interactions between the nucleus and the electrons on the same ion, and where the second term is the interaction of the nucleus with the dipolar field H_D due to the other electronic spins in the system. We have neglected quadrupole and all higher order terms. For the present system the second term is very much smaller than the first, the dipolar field having a value ≈ 4 kOe for CoF$_2$.

In order to obtain a theoretical estimate for the nuclear resonance frequency it is necessary to have a value for A_z^{59}. Ideally, this should be calculated from first principles in the manner demonstrated by Abragam and Pryce.[28] To do this, however, requires a knowledge of the proper ground state of the system which may be obtained only from a treatment of Eq. (2.1). A knowledge of the electronic "spin Hamiltonian," which we have obtained in this paper, is by itself not sufficient. We must, therefore, look for a less direct approach.

Paramagnetic resonance experiments on Co^{++} in ZnF$_2$ have recently been performed by Hensel.[29] An analysis of the hyperfine spectrum is sufficient to give an experimental value for A_z^{59} for this case. Let us make the supposition that the hyperfine interaction constants for CoF$_2$ and for Co^{++} in ZnF$_2$ are approximately equal, assuming that the crystalline field seen by Co^{++} in ZnF$_2$ is closer to that existing in CoF$_2$ than to that in ZnF$_2$.

If we include in the Hamiltonian (2.2) a hyperfine term $\mathbf{I}\cdot A^{59}\cdot\mathbf{S}$ and an external magnetic field term $-g_z\mu_BS_zH_z$, then we find, to a good approximation, eigenvalues

$$E_\pm=\pm g[g_z\mu_BH_z-A_z^{59}m], \quad (7.2)$$

where m is the quantum number associated with the nuclear spin I_z, and where g is given by Eq. (3.15) and has the value 0.77. Hensel[29] measures gg_z to be 2.11 and the hyperfine separation $2gA_z^{59}$ to be 36.8 Oe. It follows that $A_z^{59}=4.72\ 10^{-3}\ \mathrm{cm}^{-1}$.

Substituting the estimated values for H_D and A_z^{59} into (7.1), and using $\gamma^{59}\hbar=1.00$ kc/sec/Oe and $\bar{S}=1.06$ (as obtained from spin-wave theory), we calculate a zero-field nuclear resonance frequency

$$\omega_N=(141.6\bar{S}+4)\approx 154\ \mathrm{Mc/sec}. \quad (7.3)$$

This value is some 15% less than that measured experimentally.[9] We can think of no terms omitted from the calculation which will approach this order of magnitude. The term representing the direct interaction between the nucleus and the applied field H_z does not enter into the expression for the hyperfine separation. There will, it is true, be a chemical-shift term (of the type discussed by Moriya)[30] due to the interaction between the nucleus and the electron orbital moment which is produced by the polarization of the ground orbital state by the external field. For external fields of a few kilogauss as are customarily used in paramagnetic resonance experiments, the inclusion of such a term into (7.2) would change the estimated value for A_z^{59} by less than 1%.

It would seem probable, therefore, that the discrepancy is due to our assumption that the hyperfine constants for CoF$_2$ and for Co^{++} in ZnF$_2$ are the same. Lending support to this explanation is the fact that the two largest contributions to A_z^{59}, namely the electron-orbit term and the Fermi contact term, are of opposite signs, so that a relatively small change in the former (due to a small change in crystal field) may well produce a much enhanced effect on the resultant hyperfine parameter.

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