Magnetic Properties of CoCl₂ and NiCl₂

M. E. LINES

Clarendon Laboratory, University of Oxford, Oxford, England

Crystal field theory has been used to examine the origin of magnetic anisotropy in CoCl₂ and NiCl₂. These salts are antiferromagnets in which the metal ions form ferromagnetic layers with alternate layers oriented in opposite directions. An exchange Hamiltonian is derived for ions in the ground state taking account of a ferromagnetic in-layer interaction J_1 and an antiferromagnetic between-layer interaction J_2, and it is found that the anisotropy may be approximately represented by including a single extra parameter. The cooperative problem is then treated by molecular field theory at extremes of high and low temperature, and by Green function techniques (using the results of the previous paper) for temperatures near the Néel point. Fitting low-temperature experimental results with the theory, the exchange interactions are calculated showing, in particular, that the ratio J_1/J_2 is large in both salts (11.6 for CoCl₂, 13.1 for NiCl₂). Using these estimates the high-temperature susceptibility is derived and a good agreement between experiment and theory observed. For CoCl₂ the anisotropy is considerable and g values $g_{||}=3.38$ and $g_{\perp}=4.84$ are estimated.

1. INTRODUCTION

THE anhydrous chlorides of iron, cobalt, and nickel are members of a class of substances which have been widely referred to in the literature as metamagnetics. Their somewhat unorthodox magnetic properties have been investigated experimentally in some detail, and we may mention, in particular, the work of Starr, Bitter, and Kaufmann[1] on powder susceptibility; Trapeznikowa and Schubnikow[2] on specific heats; and more recently, the single-crystal susceptibility measurements of Bizette, Terrier, and Tsai[3]; and the neutron-diffraction experiments of Wilkinson, Cable, Wollan, and Koehler.[4]

For each of these salts the magnetic susceptibility in small magnetic fields shows a maximum at a temperature close to that at which a lambda-type anomaly occurs in the specific heat. This kind of magnetic behavior suggests the appearance of antiferromagnetic ordering for temperatures below the anomaly. The salts, however, are conspicuous among antiferromagnets in that the low-temperature susceptibility is quite markedly field-dependent while the paramagnetic Curie temperature Θ [obtained by applying the Curie-Weiss law $\chi = C/(T-\Theta)$ to high-temperature susceptibility measurements] is positive.

All three salts have a crystal structure of the CdCl₂ type (see Wyckoff[5]) in which the metal ions are arranged in hexagonal layers, where each layer is separated from an adjacent one by two hexagonal layers of chlorine anions. As long ago as 1933, Landau[6] suggested that the magnetic properties could be qualitatively explained if there were present a strong ferromagnetic intralayer interaction together with a much smaller antiferromagnetic interlayer interaction. Thus, in the ordered state, this would give rise to ferromagnetically ordered layers with the magnetic moments of alternate layers oriented in opposite directions. The weakness of the antiferromagnetic exchange could account for a field dependence of susceptibility in the ordered state, and the dominant ferromagnetic exchange would lead us to expect a ferromagnetic "internal field" and, thus, a positive value of Θ.

To put these ideas on a more rigorous basis, Néel[7] applied the molecular-field theory to the problem, and was able to give a semiquantitative explanation of many of the magnetic properties. The major difficulties which present themselves when one attempts a more quantitative theoretical treatment of the problem are twofold. Firstly, we must necessarily include two different exchange parameters in order to describe the interactions between nearest neighbors (in-plane) and between next-nearest neighbors (between-plane). This makes any cluster treatment of the problem difficult. In addition, however, the magnetic properties indicate that the salts are, by no means, isotropic, and that, in particular, the anisotropy for FeCl₂ and CoCl₂ is very considerable. This means that before we can attempt the cooperative problem, it is necessary to examine the microscopic origin of the anisotropy in order to determine the form of the anisotropic part of the Hamiltonian. This has been done for FeCl₂ by Kanamori,[8] who concludes that at temperatures near or below its Néel point this salt behaves, to a good approximation, as an Ising antiferromagnet with the hexagonal axis c_0 as the preferred direction of spin alignment. Thus, for this case, the inclusion of anisotropy provides a relative simplification of the problem, and both Yomosa[9] and Heap[10] have used the Bethe-Peierls cluster method to attack the Ising problem. They are able to obtain a good agreement between theory and experiment if the ferromagnetic intralayer exchange, J_1, is considerably larger than the antiferromagnetic interlayer exchange,

[1] C. Starr, F. Bitter, and A. R. Kaufmann, Phys. Rev. **58**, 977 (1940).

[2] O. N. Trapeznikowa and L. W. Schubnikow, Physik. Z. Sowjetunion **7**, 66 (1935).

[3] H. Bizette, C. Terrier and B. Tsai, Compt. Rend. **243**, 1295 (1956).

[4] M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, Phys. Rev. **113**, 497 (1959).

[5] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers Inc., New York, 1948).

[6] L. Landau, Physik. Z. Sowjetunion **4**, 675 (1933).

[7] L. Néel, Suppl. Nuovo Cimento **6**, 942 (1957).

[8] J. Kanamori, Progr. Theoret. Phys. (Kyoto) **20**, 890 (1958).

[9] S. Yomosa, J. Phys. Soc. Japan **15**, 1068 (1960).

[10] B. R. Heap, Proc. Phys. Soc. (London) **80**, 248 (1962).

J_2. Heap[10] finds that the best fit is obtained when $J_1/J_2 = 12.4$.

Kanamori[8] also gives a brief outline of the situation for CoCl₂ and NiCl₂. In both these salts he indicates that the anisotropy is such that the preferred direction of spin alignment is normal to the c_0 axis. Such a direction is also indicated by the magnetic-susceptibility experiments, and has been confirmed in the case of the cobalt salt by neutron-diffraction experiments (Wilkinson et al.[4]).

In the present paper we shall make a detailed investigation of the microscopic origin of the anisotropy energy for CoCl₂ and NiCl₂ (using crystal field theory) and in this way we shall find the form of the exchange Hamiltonian in each case. The cooperative problem, using a Hamiltonian of the derived form, we have treated by the method of double-time Green functions in the preceding paper. Using the experimental information which is available concerning low-field, low-temperature susceptibility and the Néel temperature, we find that we are able, by fitting theory to experiment, to deduce values for the isotropic and anisotropic exchange interactions in the cobalt and nickel salts. Using these values, we go on to evaluate the high-temperature susceptibility and find good agreement of theory with experiment.

2. CRYSTAL FIELD THEORY, CoCl₂

Using the one-ion approximation and the weak-field coupling scheme, we consider a single Co⁺⁺ ion in the crystal field of the rest of the lattice. The crystal structure is such that the cobalt ion is surrounded by a distorted octahedron of Cl⁻ ions, in which the distortion is a trigonal one (along the c_0 axis). The lowest orbital states of the free Co⁺⁺ ion (derived from the electronic configuration $3d^7$) are ^4F and ^4P in that order, the energy separation being $\sim 14\,000$ cm⁻¹. No other terms of the same symmetry arise from $3d^7$, and other configurations give terms which are energetically far higher so that we may neglect them.

In a cubic crystal field, the ^4F state is split into two orbital triplets and one orbital singlet, with a triplet lowest. If the trigonal c_0 axis is chosen to be the axis of quantization with wave functions ϕ_m, where $m\hbar$ denotes the component of angular momentum in the direction of the axis, then the states may be written (see, for example, Bleaney and Stevens[11])

Energy Symmetry   Wave function

6Δ $^4A_2$ $(\sqrt{2}/3)(\phi_3 - \phi_{-3}) - (\sqrt{5}/3)\phi_0$

Δ $^4T_2$ $\begin{cases} (1/\sqrt{2})(\phi_3 + \phi_{-3}) \\ (1/\sqrt{6})\phi_2 - (\sqrt{5}/\sqrt{6})\phi_{-1} \\ (1/\sqrt{6})\phi_{-2} + (\sqrt{5}/\sqrt{6})\phi_1 \end{cases}$, (2.1)

-3Δ $^4T_1$ $\begin{cases} (2/3)\phi_0 - (\sqrt{5}/3\sqrt{2})(\phi_3 - \phi_{-3}) \\ (\sqrt{5}/\sqrt{6})\phi_2 + (1/\sqrt{6})\phi_{-1} \\ (\sqrt{5}/\sqrt{6})\phi_{-2} - (1/\sqrt{6})\phi_1 \end{cases}$

[11] B. Bleaney and K. W. H. Stevens, Rept. Progr. Phys. **16**, 107 (1953).

where we have labeled the states according to their symmetry group (see Griffith[12]) and where Δ is an energy parameter which is positive for CoCl₂. The magnitude of Δ may be obtained by interpreting optical-resonance data and for CoCl₂ is in the region 1600 cm⁻¹ to 1700 cm⁻¹ (Jones[13]). The free-ion ^4P term is not split by the cubic field and remains an orbital triplet with symmetry group $^4T_1$. Since the ^4P term and the ground-orbital triplet have the same symmetry, however, the cubic field mixes a little of the former into the ground state.

The result of this ^4P admixture is to reduce the matrix elements of the orbital angular momentum $\mathbf{L}$ from the values which would be obtained by using the pure $^4T_1(^4F)$ wave functions (see, for example, Abragam and Pryce[14]). This reduction, however, will not be an isotropic one for CoCl₂ since there exists in this salt a considerable trigonal distortion which we have not yet introduced. A further considerable reduction of $\mathbf{L}$ is caused by the bonding of the cation orbitals with those of neighbor chlorine anions resulting in the distortion of the pure d orbitals of $^4T_1(^4F)$. This effect has been considered in some detail by Tinkham[15] who replaces $\mathbf{L}$ by $k\mathbf{L}$ where the value of k is less than but of order unity. In this paper we shall take a factor k to include all the reduction thus neglecting any anisotropy introduced by the $^4T_1(^4P)$ admixture. We shall, therefore, replace $\mathbf{L}$ by $k\mathbf{L}$ in the matrix elements which will be evaluated by taking the ground-orbital state to be $^4T_1(^4F)$.

Consider this ground-orbital triplet. Let us write

$$\begin{aligned} |-1\rangle &= (\sqrt{5}/\sqrt{6})\phi_2 + (1/\sqrt{6})\phi_{-1}, \\ |\ 0\rangle &= (2/3)\phi_0 - (\sqrt{5}/3\sqrt{2})(\phi_3 - \phi_{-3}), \quad (2.2) \\ |+1\rangle &= (\sqrt{5}/\sqrt{6})\phi_{-2} - (1/\sqrt{6})\phi_1. \end{aligned}$$

We may easily verify that

$$\langle \pm 1 | L_z | \pm 1 \rangle = \mp \tfrac{3}{2}, \quad \langle 0 | L_z | 0 \rangle = 0 \quad (2.3)$$

and, in fact, we may further show that all the matrix elements of $\mathbf{L}$ within the above states of $^4T_1$ are exactly the same as the matrix elements of $-3\mathbf{L}/2$ between the associated P functions. In group theoretical language we refer to the structural isomorphism of $^4T_1$ with ^4P (Griffith[12]).

So far we have included in the calculation only the cubic part of the crystal field. We are now in a position to introduce the trigonal distortion, together with the spin-orbit coupling, as a perturbation within the twelve states of the effective P state which we shall label $|m_L, m_S\rangle$ where the spin S is $\tfrac{3}{2}$.

The trigonal distortion is defined by its eigenstates

[12] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, London, 1961).
[13] G. D. Jones (private communication).
[14] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A206**, 173 (1951).

and eigenvalues which we shall write

$$\langle 0,m_S | V(\text{trig}) | 0,m_S \rangle = 2\delta/3,$$
$$\langle \pm 1,m_S | V(\text{trig}) | \pm 1,m_S \rangle = -\delta/3. \tag{2.4}$$

Including both the spin-orbit coupling and the trigonal distortion, we may now write our perturbing Hamil-

tonian in the form

$$\mathcal{3C} = -\tfrac{3}{2}k\lambda \mathbf{L}\cdot\mathbf{S} - \delta(L_z^2 - \tfrac{2}{3}), \tag{2.5}$$

where λ is the spin-orbit coupling constant and may differ from its free-ion value of -180 cm^{-1}. The matrix of spin-orbit coupling and trigonal field within the ground $^4T_1$ term is, therefore, found by evaluating the matrix elements of the Hamiltonian (2.5) within the effective P state $|m_L,m_S\rangle$. We find, where $\lambda'=k\lambda$,

	$\|-1,\tfrac{3}{2}\rangle$	$\|0,\tfrac{1}{2}\rangle$	$\|1,-\tfrac{1}{2}\rangle$	$\|0,\tfrac{3}{2}\rangle$	$\|1,\tfrac{1}{2}\rangle$	$\|1,\tfrac{3}{2}\rangle$
$\langle-1,\tfrac{3}{2}\|$:	$-\tfrac{1}{3}\delta+(9/4)\lambda'$	$-\tfrac{9}{2}(1/\sqrt{6})\lambda'$	0	0	0	0
$\langle 0,\tfrac{1}{2}\|$:	$-\tfrac{9}{2}(1/\sqrt{6})\lambda'$	$\tfrac{2}{3}\delta$	$-(3/\sqrt{2})\lambda'$	0	0	0
$\langle 1,-\tfrac{1}{2}\|$:	0	$-(3/\sqrt{2})\lambda'$	$-\tfrac{1}{3}\delta+\tfrac{3}{4}\lambda'$	0	0	0
$\langle 0,\tfrac{3}{2}\|$:	0	0	0	$\tfrac{2}{3}\delta$	$-\tfrac{9}{2}(1/\sqrt{6})\lambda'$	0
$\langle 1,\tfrac{1}{2}\|$:	0	0	0	$-\tfrac{9}{2}(1/\sqrt{6})\lambda'$	$-\tfrac{1}{3}\delta-\tfrac{3}{4}\lambda'$	0
$\langle 1,\tfrac{3}{2}\|$:	0	0	0	0	0	$-\tfrac{1}{3}\delta-(9/4)\lambda'$

$$(2.6)$$

the matrix elements for $|-m_L,-m_S\rangle$ being the same as those for $|m_L,m_S\rangle$. The $^4T_1(^4F)$ state, therefore, splits into six Kramers doublets, and we may solve the secular equation to give their energies as functions of δ/λ'. The secular equation reduces to three separate equations for energy, one linear (E_l), one quadratic (E_q), and one cubic (E_c), and we show the solutions graphically in Fig. 1. For all values of δ/λ' the same E_c solution lies lowest and we may write the wave functions for this doublet

$$\psi_{+1}=c_1|-1,\tfrac{3}{2}\rangle+c_2|0,\tfrac{1}{2}\rangle+c_3|1,-\tfrac{1}{2}\rangle,$$
$$\psi_{-1}=c_1|1,-\tfrac{3}{2}\rangle+c_2|0,-\tfrac{1}{2}\rangle+c_3|-1,\tfrac{1}{2}\rangle, \tag{2.7}$$

where the coefficients c_1, c_2, c_3, are determined by the value of δ/λ' applicable to CoCl$_2$ which we shall estimate later.

We now introduce an external magnetic field, H_0, and examine the resulting shift of the energy levels by perturbation theory. We shall consider, in particular, the splitting of the lowest Kramers doublet by this perturbation operator, which we may write

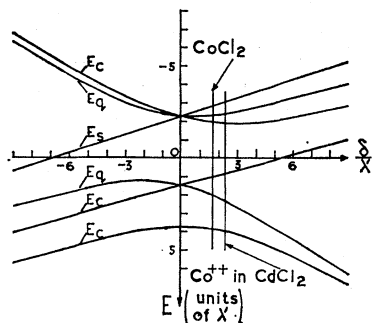$$\beta H_0(-\tfrac{3}{2}k\mathbf{L}+2\mathbf{S}), \tag{2.8}$$

where β is the Bohr magneton. Let us first consider the case of H_0 parallel to the trigonal axis $c_0(z)$. Using perturbation theory within the ground Kramers doublet, we find energy shifts

$$\langle\psi_{\pm 1}|(-\tfrac{3}{2}kL_z+2S_z)|\psi_{\pm 1}\rangle\beta H_0. \tag{2.9}$$

If we write this in terms of an effective spin $\tfrac{1}{2}$ as $\pm\tfrac{1}{2}\beta g_{\parallel}H_0$, thus defining a g factor for this direction, we have, using (2.7) and (2.9),

$$g_{\parallel}=(6+3k)c_1^2+2c_2^2-(3k+2)c_3^2. \tag{2.10}$$

In a similar way, when H_0 is perpendicular to c_0, we may define a g factor $g_\perp$ which is given by

$$g_\perp=\langle\psi_{\pm 1}|[-\tfrac{3}{2}k(L^++L^-)+2(S^++S^-)]|\psi_{\mp 1}\rangle, \tag{2.11}$$

where $L^\pm=L_x\pm iL_y$, $S^\pm=S_x\pm iS_y$. It follows that

$$g_\perp=4c_2^2+4\sqrt{3}c_1c_3-3\sqrt{2}kc_2c_3. \tag{2.12}$$

We noted above that the secular equation for the ground state was cubic. Following Abragam and Pryce,[14] we may obtain a parametric solution by introducing the parameter x, defined by

$$E_c=-\delta/3+\tfrac{3}{4}\lambda'(x+3). \tag{2.13}$$

It follows that

$$c_1:c_2:c_3=(\sqrt{6}/x):-1:[\sqrt{8}/(x+2)] \tag{2.14}$$

and

$$\delta/\lambda'=\tfrac{3}{4}(x+3)-(9/2x)-6/(x+2). \tag{2.15}$$

Using (2.10) and (2.12), we may express $g_{\parallel}$ and $g_\perp$ in terms of x and k alone. We find

$$g_{\parallel}=\frac{(6/x^2)(6+3k)+2-[8/(x+2)^2](2+3k)}{(6/x^2)+1+8/(x+2)^2}, \tag{2.16}$$

$$g_\perp=\frac{4[1+12/x(x+2)+3k/(x+2)]}{(6/x^2)+1+8/(x+2)^2}. \tag{2.17}$$

Fig. 1. The splitting of the ground orbital triplet $^4T_1(^4F)$ by the spin-orbit coupling (λ') and the trigonal field (δ). The values of δ/λ' which occur for Co^{++} in CdCl$_2$ and for Co^{++} in CoCl$_2$ are indicated in the figure.

In these results, however, we have neglected the effects of spin-orbit coupling in admixing the upper orbital levels into the ground-state orbital triplet $^4T_1$. The largest mixing comes from the $^4T_2(^4F)$ state, and in the simple approximation of no trigonal distortion this adds to both the g values a term $(-15/2)\lambda'/\Delta'$ where Δ' is the energy separation between the two triplet states of ^4F and has a value $\sim$6600 cm^{-1} (Jones[13]) for CoCl₂. A more accurate evaluation of the total correction can be made (see, for example, Abragam and Pryce[14]) provided that one possesses a detailed knowledge of the optical spectrum. With such a correction, a measurement of the g values is sufficient to determine x and k.

At the present time, however, we do not possess a detailed knowledge of the optical spectrum for CoCl₂, neither are we aware of a published measurement of the g values. (A measurement of the g values for CoCl₂ is likely to be difficult since the salt becomes antiferromagnetic in that region of temperature where the spin-lattice relaxation time would be most favorable for the performance of resonance experiments.) We must, therefore, proceed by a less direct method.

We shall assume the value $k=0.9$ (compare Tinkham[15] for Co^{++} in ZnF₂, and Low[16] for Co^{++} in MgO) which should be a fair estimate for the effect of bonding with the Cl$^-$ anions but which largely neglects the (possibly strongly anisotropic) effect of cubic-field ^4P admixture. The small spin-orbit correction to the g values we shall take to be 0.15 for both $g_{\parallel}$ and $g_{\perp}$. We are left with only one parameter (x) and we shall show that we are able to estimate its value in CoCl₂ by examining the bulk magnetic properties of the salt.

We may quickly get some idea of the approximate magnitude of x by considering the case of Co^{++} in CdCl₂ for which we do have experimental information[17] as follows: $g_{\parallel}=3.04$, $g_{\perp}=4.95$. Using the above estimates for k and for the spin-orbit correction to the g values we may put $g_{\parallel}$ and $g_{\perp}$ [from (2.16) and (2.17)] equal to 2.89 and 4.80, respectively, and deduce that for this case $x \doteq 3.4$, giving, from (2.15), $\delta/\lambda'=2.37$ (see Fig. 1).

We should expect the value of δ/λ' for CoCl₂ to be not too far removed from this value for Co^{++} in CdCl₂, and thus, from Fig. 1, we see that there is likely to be an energy gap of at least $1.5\lambda'$ (which is probably $\sim$300°K) between the two lowest Kramers doublets. For an analysis of the magnetic properties of CoCl₂ near and below its Néel temperature $T_N=25$°K, we may, therefore, safely assume that the ions are predominantly in the ground state. For an ion in this ground state we may, using Eq. (2.7), readily show that the matrix elements of S_x, S_y, and S_z are,

[15] M. Tinkham, Proc. Roy. Soc. (London) **A236**, 549 (1956).
[16] W. Low, Phys. Rev. **109**, 256 (1958).
[17] K. Morigaki, J. Phys. Soc. Japan **16**, 1639 (1961).

respectively,

$$
\begin{array}{cc}
 & \psi_1 \quad \psi_{-1} \\
\hline
\psi_1: & 0 \qquad q \\
\psi_{-1}: & q \qquad 0
\end{array}
\qquad
\begin{array}{cc}
 & \psi_1 \quad \psi_{-1} \\
\hline
\psi_1: & 0 \qquad -iq \\
\psi_{-1}: & iq \qquad 0
\end{array}
\qquad
\begin{array}{cc}
 & \psi_1 \quad \psi_{-1} \\
\hline
\psi_1: & p \qquad 0 \\
\psi_{-1}: & 0 \qquad -p
\end{array}
\qquad (2.18)
$$

where

$$p=\tfrac{3}{2}c_1^2+\tfrac{1}{2}c_2^2-\tfrac{1}{2}c_3^2, \qquad (2.19)$$

$$q=c_2^2+\sqrt{3}c_1c_3, \qquad (2.20)$$

so that we may formally replace the true spin $S=\tfrac{3}{2}$, within the ground doublet, by a spin-half operator, **s**, where

$$S_x=2qs_x, \quad S_y=2qs_y, \quad S_z=2ps_z. \qquad (2.21)$$

We may note that for the case of extreme trigonal splitting ($\delta \gg \lambda'$) $c_2=1$, $c_1=c_3=0$; $p=\tfrac{1}{2}$, $q=1$, and that for the case of negligible trigonal field $c_1=1/\sqrt{2}$, $c_2=-1/\sqrt{3}$, $c_3=1/\sqrt{6}$; $p=q=\tfrac{5}{6}$.

3. THE MAGNETIC PROPERTIES

Let us now consider the Heisenberg exchange operator $\mathcal{H}_{ij}=J'\mathbf{S}_i \cdot \mathbf{S}_j$. In the ground doublet we may write, using (2.21)

$$\mathcal{H}_{ij}=J'[\alpha_{\parallel}^2 s_{iz}s_{jz}+\alpha_{\perp}^2(s_{ix}s_{jx}+s_{iy}s_{jy})] \qquad (3.1)$$

in terms of the spin operator, **s**, where

$$\alpha_{\parallel}=3c_1^2+c_2^2-c_3^2, \qquad (3.2)$$

$$\alpha_{\perp}=2c_2^2+2\sqrt{3}c_1c_3. \qquad (3.3)$$

For treatment of the cooperative problem it is convenient to single out the preferred direction of antiferromagnetic alignment as a z axis, and since, for both CoCl₂ and NiCl₂, this direction is normal to the hexagonal c_0 axis, we shall define a new set of coordinates as follows: Let the preferred direction of ordering be z', the direction of the c_0 axis be x', and let y' be chosen to complete the orthogonal set. In this notation we may write (3.1) as

$$\mathcal{H}_{ij}=J\mathbf{s}_i \cdot \mathbf{s}_j - Ds_{ix'}s_{jx'}, \qquad (3.4)$$

where

$$J=\alpha_{\perp}^2 J', \quad \text{and} \quad D=(\alpha_{\perp}^2-\alpha_{\parallel}^2)J', \qquad (3.5)$$

giving

$$\frac{D}{J}=\frac{\alpha_{\perp}^2-\alpha_{\parallel}^2}{\alpha_{\perp}^2}. \qquad (3.6)$$

For CoCl₂ we introduce a ferromagnetic exchange J_1, D_1 between nearest neighbors, together with an antiferromagnetic exchange J_2, D_2 between next-nearest neighbors, assuming that the anisotropy introduced by D_1 and D_2 is sufficient to provide a fair representation of the total anisotropy of the salt; that is, we assume that it far outweighs other sources of anisotropy such as the dipole-dipole coupling.

In this representation, we write the total exchange Hamiltonian

$$\mathcal{3C}=\sum_{nn}\left[-J_1\mathbf{s}_i\cdot\mathbf{s}_j+D_1s_{ix'}s_{jx'}\right]+$$

$$\sum_{nnn}\left[J_2\mathbf{s}_i\cdot\mathbf{s}_j-D_2s_{ix'}s_{jx'}\right], \quad (3.7)$$

where we have chosen the signs so that all the parameters are positive for $CoCl_2$. From (3.6) we see that we may write

$$(D_1/J_1)=(D_2/J_2)=(\alpha_\perp^2-\alpha_{||}^2)/\alpha_\perp^2, \quad (3.8)$$

where $\alpha_{||}$ and $\alpha_\perp$ are both functions of x, so that we have reduced the problem to the evaluation of three unknowns J_1, J_2, and x. In order to obtain estimates for these quantities, we shall use the experimental results for the Néel temperature T_N and for the magnetic susceptibilities parallel ($\chi_{||}$) and perpendicular ($\chi_\perp$) to c_0 at temperatures below T_N. We shall use the susceptibility measurements of Bizette, Terrier, and Tsai.[3] They measure $\chi_{||}$ and $\chi_\perp$ from very low temperatures up to $\sim300°K$ using magnetic fields of several kilogauss. Wilkinson et al.[4] shows that the anisotropy within the c_0 plane [which has been neglected in (3.7)] is so small that only a few kilogauss is required, at temperatures below T_N, to align nearly all spins normal to a magnetic field applied in this plane. It is, thus, fairly safe to assume that Bizette's in-plane measurement is, like the one made along the c_0 direction, a measurement of susceptibility perpendicular to the direction of spin alignment. For $T<T_N$ Bizette[3] finds the susceptibilities almost independent of temperature with values (per mole) of $\chi_\perp=0.4$, $\chi_{||}=0.06$. Theoretically it is quite simple to evaluate this susceptibility at temperatures below T_N since it is well known (see, for example, Ziman[18]) that the spin-wave theory, which is a good approximation at very low temperatures, gives for this quantity the same result as the simple molecular-field theory. We shall, therefore, use the molecular-field theory, treating the spin as a classical vector.

Consider first the magnetic field H_0 applied parallel to c_0. In the absence of the field the spins are aligned antiferromagnetically in a direction contained in the c_0 plane. Since each spin has six parallel nearest neighbors and six antiparallel next-nearest neighbors, the total exchange energy of the lattice of N spins is

$$E_0=-3N(J_1+J_2)S^2. \quad (3.9)$$

When the field H_0 is applied, let all the spins turn through a small angle ϕ towards the direction of c_0. (We assume that H_0 is small compared with the internal field.) The energy of the system is now, to second order in ϕ,

$$E=E_0-Ng_{||}\beta H_0S\phi+3NS^2\phi^2(2J_2+D_1-D_2). \quad (3.10)$$

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[18] J. M. Ziman, Proc. Phys. Soc. (London) A65, 540, 548 (1952).

The equilibrium value of ϕ is found by making $E-E_0$ an extremum, giving

$$\phi=g_{||}\beta H_0/(2J_2+D_1-D_2)6S. \quad (3.11)$$

But the total magnetization is $NS\phi g_{||}\beta$ and, hence, the susceptibility is given by

$$\chi_{||}=Ng_{||}^2\beta^2/6(2J_2+D_1-D_2). \quad (3.12)$$

In an exactly similar way we may evaluate the in-plane susceptibility and we find

$$\chi_\perp=Ng_\perp^2\beta^2/12J_2. \quad (3.13)$$

In order to obtain a theoretical estimate for T_N in terms of J_1, J_2, and D/J we use Fig. 2 of the preceding paper (which we shall refer to as paper A) which has been obtained by applying the method of double-time Green functions to a Hamiltonian of the form (3.7). Experimentally T_N is found to be close to 25°K.

We now consider values of x in the region $x\sim3$ since we anticipate that the value of x applicable to $CoCl_2$ will not be far removed from the value ($\doteq3.4$) which was found for Co^{++} in $CdCl_2$. Choosing a particular value ($x=3.0$, say) we may calculate D/J using Eqs. (2.14), (3.2), (3.3), and (3.6). We find that $D/J=0.446$. But we may also calculate this same quantity using the experimental values for $\chi_{||}$, $\chi_\perp$, and T_N together with the theoretical results of (3.12), (3.13) [where for $g_{||}$ and $g_\perp$ we use Eqs. (2.16), (2.17) not forgetting to include the correction for the second-order spin-orbit coupling] and the Green function graph from paper A. We find $D/J=0.41$ and, therefore, the methods are not consistent for this particular value of x. Trying other values for x we may again obtain values for D/J by these two methods, and we obtain the results shown graphically in Fig. 2. We find consistency for a value of x close to 2.92. We, therefore, use this value of x for $CoCl_2$ and proceed to estimate,

from (2.16)	$g_{||}=3.23+0.15=3.38$
from (2.17)	$g_\perp=4.69+0.15=4.84$
from (2.14)	$c_1:c_2:c_3=0.839:-1:0.575$
from (2.15)	$\delta/\lambda'=1.68$ (see Fig. 1)
from (3.13)	$J_2=1.79°K$
from (3.6)	$D/J=0.425$
from (3.12)	$D_1=8.82°K$

and, hence, $J_1=20.8°K$, $D_2=0.76°K$, and $J_1/J_2=11.6$.

4. NiCl₂

We now consider the situation in $NiCl_2$ which, like $CoCl_2$, has the $CdCl_2$ crystal structure, and almost certainly has the same antiferromagnetic spin pattern as the cobalt salt. The task of predicting the exchange interactions for this salt is somewhat simpler than was the case for $CoCl_2$. This is primarily because, as we shall

see below, the Hamiltonian is far less anisotropic in this case.

The free Ni^{++} ion has a ^3F term lowest and this splits in the cubic field exactly as did the ^4F state for the cobalt salt, except that for nickel the energy parameter Δ is negative, which makes the orbital singlet term lowest. In this ground-orbital singlet, the mean value of orbital angular momentum is zero and the value of spin $S=1$. The level is, thus, triply degenerate and would remain so under the influence of either spin-orbit coupling alone, or trigonal field alone. Anisotropy arises only as a second-order effect though the combined effect of spin-orbit coupling and trigonal field within the upper states which are linked with the ground state in the second-order perturbation. The problem of describing the splitting of the ground term for nickel in a distorted octahedral environment has been considered by Stevens.[19] For a trigonal distortion, we expect the anisotropy to be adequately represented simply by a term DS_z^2. For Ni^{++} in $CdCl_2$ we have experimental information (Orton[20]) who reports that $D=1.41$ cm⁻¹, favoring the c_0 plane. For $NiCl_2$ itself we should expect a very similar result.

The other main source of anisotropy in $NiCl_2$ is the interspin dipole-dipole interaction. This amounts to ~ 0.5 cm⁻¹/spin between the c_0 axis and the plane (Kanamori[8]) again favoring the plane. Experimentally the g value is found to be isotropic[21] ($g=2.25\pm0.02$; anomalous values reported for $T<50°K$ are probably due to the onset of long-range order), and also, no anisotropy is detected in susceptibility experiments.[3] This suggests that the anisotropy energy is extremely small compared with the isotropic exchange interaction energy. We, therefore, neglect it entirely, using the Hamiltonian (3.7) but putting $D_1=D_2=0$. Using the experimental results for Néel temperature (50°K) and for the magnetic susceptibility below T_N ($\chi_{11}=\chi_\perp$ $\doteqdot 0.107$) and comparing them with the theoretical results of Eq. (3.13) and the isotropic spin 1 curve of Fig. 2 in paper A, we obtain estimates for the exchange interactions in $NiCl_2$, as follows:

$$J_1=19.0°K, \quad J_2=1.45°K,$$

giving

$$J_1/J_2=13.1.$$

Thus, the results obtained in the present paper, together with the results of the Ising theory for $FeCl_2$ by Heap,[10] would seem to suggest that the ratio of ferromagnetic to antiferromagnetic exchange is very similar in each of the metamagnetics $FeCl_2$, $CoCl_2$, and $NiCl_2$. The theories give, respectively, J_1/J_2 equal to 12.4, 11.6, and 13.1.

[19] K. W. H. Stevens, Proc. Roy. Soc. (London) **A214**, 237 (1952).
[20] J. W. Orton, Rept. Progr. Phys. **22**, 204 (1959).
[21] J. W. Leech and A. J. Manuel, Proc. Phys. Soc. (London) **B69**, 210 (1956).

FIG. 2. Curve (i) shows the values of D/J calculated from crystal field theory as a function of the parameter x of Eq. (2.13). Curve (ii) shows the same quantity calculated from the bulk magnetic properties of $CoCl_2$. The point of intersection, giving the value of x applicable to $CoCl_2$, is at $x=2.92$.
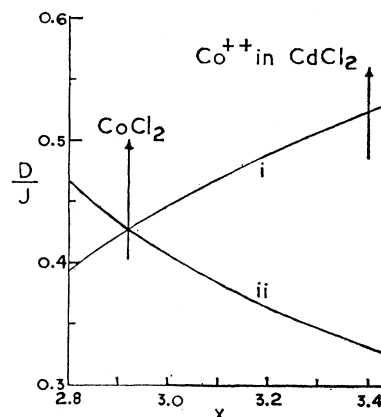
5. HIGH-TEMPERATURE SUSCEPTIBILITY

Having made estimates of the dominant exchange interactions in both $CoCl_2$ and $NiCl_2$, we may now proceed to check these values by calculating the high-temperature magnetic susceptibility in each case and comparing the results with experiment. Since we shall be concerned mainly with temperatures many times the transition temperature, we shall expect the simple molecular field theory to be adequate. We shall first calculate the susceptibility assuming all ions to be in the same state, a state for which we may write a Hamiltonian of the form (3.7). This will be an adequate approximation for the nickel salt, but will be very poor for $CoCl_2$ for temperatures much above 100°K.

We introduce a magnetic field H_0 in a direction r making an angle θ with the c_0 axis. In the molecular-field approximation we may write the Hamiltonian for the ith spin

$$\mathcal{H}_i = \left(\sum_{nnn} J_2 - \sum_{nn} J_1\right)s_{ir}\bar{s}_j + \left(\sum_{nn} D_1 - \sum_{nnn} D_2\right)$$

$$\times \cos^2\theta s_{ir}\bar{s}_j - g_\theta\beta H_0 s_{ir}), \quad (5.1)$$

where $\sum_{nn}(\sum_{nnn})$ means the sum over all spins $\bar{s}_j$ which are nearest neighbors (next-nearest neighbors) of s_i, where the $\bar{s}_j$ are now average values in the direction of H_0, and where

$$g_\theta = g_{11}\cos^2\theta + g_\perp\sin^2\theta. \quad (5.2)$$

The ith spin is now in an "effective field" H_i given by

$$H_i = H_0 - V_i/g_\theta\beta s_{ir}, \quad (5.3)$$

where

$$V_i = \left(\sum_{nnn} J_2 - \sum_{nn} J_1\right)s_{ir}\bar{s}_j + \left(\sum_{nn} D_1 - \sum_{nnn} D_2\right)$$

$$\times \cos^2\theta s_{ir}\bar{s}_j. \quad (5.4)$$

For temperatures above the Néel point where $g_\theta\beta H_i S \ll kT$ (S is the spin quantum number and k Boltzmann's constant) the simple theory of paramagnetism for

spins s_i in a field H_i gives

$$\bar{s}_i = g_\theta \beta S(S+1) H_i / 3kT. \tag{5.5}$$

If we now introduce two sublattices "a" and "b" upon which the spins in the ordered state are, respectively, "up" and "down," we have, from (5.3), (5.4), and (5.5)

$$\bar{s}_a + \bar{s}_b = \frac{g_\theta \beta S(S+1)}{3kT} \Big\{ 2H_0$$

$$- \frac{6}{g_\theta \beta}[J_2 - J_1 + (D_1 - D_2)\cos^2\theta](\bar{s}_a + \bar{s}_b) \Big\} \tag{5.6}$$

from which the total magnetization is given by

$$M = \frac{Ng_\theta\beta}{2}(\bar{s}_a + \bar{s}_b) = \frac{Ng_\theta^2\beta^2 S(S+1)H_0}{3k(T-\Theta)}, \tag{5.7}$$

where

$$k\Theta = -2S(S+1)[J_2 - J_1 + (D_1 - D_2)\cos^2\theta]. \tag{5.8}$$

We may apply this result directly to the case of $NiCl_2$ putting $D_1 = D_2 = 0$. Using the values previously obtained for the exchange parameters we find that $\Theta = 70°K$ and is independent of the angle θ. The experiments of Bizette[3] show that at high temperatures the molar susceptibility is isotropic and given by $1.33/(T-67)$, from which it follows $g_\theta = 2.25$, and $\Theta = 67°K$. The agreement is quite a good one.

$NiCl_2$, thus, provides us with a good example of a "simple" metamagnet; simple in the sense that, as far as the interpretation of bulk magnetic properties is concerned, we may represent its cooperative interactions by isotropic Heisenberg exchange terms alone. It is a point of some interest that for such a "simple" metamagnet the molecular field theory does not allow values of $\theta/T_N \geq 1$, in conflict with the observed ratio for $NiCl_2$ of 1.4. That the present theory is able to reproduce this ratio quantitatively follows very simply from the fact that the Green function method gives the same value for θ as the molecular-field theory but gives a significantly lower T_N.

Once again we find that $CoCl_2$ presents theoretically a rather more difficult problem. In this salt, the energy gap between the ground doublet and the next lowest level is (see Fig. 1) $1.8\lambda'$, where λ' is probably $\sim -200°K$. (Later in the paper we shall estimate λ' and find a value $-230°K$.) In the region of room temperature we shall, therefore, expect significant contributions to the susceptibility from states other than the ground one. We shall include in the following calculation all the six Kramers doublets which arise from the state $^4T_1(^4F)$ of the cubic field terms.

Let us, for the moment, neglect the exchange interaction. Using the values for x and δ/λ' obtained in Sec. 3, we may calculate from the secular matrix (2.6) the wave functions and energies of the ground six doublets.

They are

$$\psi_{\pm1} = 0.59|\mp1, \pm\tfrac{3}{2}\rangle - 0.70|0, \pm\tfrac{1}{2}\rangle + 0.40|\pm1, \mp\tfrac{1}{2}\rangle,$$

$$\psi_{\pm2} = 0.88|0, \pm\tfrac{3}{2}\rangle - 0.47|\pm1, \pm\tfrac{1}{2}\rangle,$$

$$\psi_{\pm3} = -0.74|\mp1, \pm\tfrac{3}{2}\rangle - 0.26|0, \pm\tfrac{1}{2}\rangle + 0.62|\pm1, \mp\tfrac{1}{2}\rangle,$$

$$\psi_{\pm4} = -0.34|\mp1, \pm\tfrac{3}{2}\rangle - 0.67|0, \pm\tfrac{1}{2}\rangle - 0.67|\pm1, \mp\tfrac{1}{2}\rangle,$$

$$\psi_{\pm5} = 0.47|0, \pm\tfrac{3}{2}\rangle + 0.88|\pm1, \pm\tfrac{1}{2}\rangle,$$

$$\psi_{\pm6} = |\pm1, \pm\tfrac{3}{2}\rangle, \tag{5.9}$$

with associated energies $E_1 = 3.88\lambda'$, $E_2 = 2.11\lambda'$, $E_3 = 1.06\lambda'$, $E_4 = -1.93\lambda'$, $E_5 = -2.30\lambda'$, and $E_6 = -2.81\lambda'$.

Introducing a magnetic field H_0 we may calculate the new energy levels by perturbation theory using the perturbing operator of Eq. (2.8) (where $k = 0.9$). For H_0 parallel to $z(c_0)$ we find, for the matrix elements of $V_{||} = (-1.35L_z + 2S_z)\beta H_0$, the values (in units of βH_0)

	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6
ψ_1:	1.62	0	-2.30	0.23	0	0
ψ_2:	0	2.25	0	0	1.39	0
ψ_3:	-2.30	0	1.55	2.24	0	0
ψ_4:	0.23	0	2.24	-0.10	0	0
ψ_5:	0	1.39	0	0	0.39	0
ψ_6:	0	0	0	0	0	1.65

$$\tag{5.10}$$

where the matrix elements for ψ_{-i} are the same as those for ψ_i and where all the other matrix elements are zero. For H_0 perpendicular to z, we find for the matrix elements of $V_\perp = [-0.68(L^+ + L^-) + (S^+ + S^-)]\beta H_0$, the values (in units of βH_0)

	ψ_1	ψ_{-2}	ψ_3	ψ_4	ψ_{-5}	ψ_6
ψ_{-1}:	2.34	-2.26	1.00	-0.18	0.46	0
ψ_2:	-2.26	0	-0.47	-0.41	0	-1.66
ψ_{-3}:	1.00	-0.47	-1.14	1.07	1.43	0
ψ_{-4}:	-0.18	-0.41	1.07	0.82	-1.00	0
ψ_5:	0.46	0	1.43	-1.00	0	1.07
ψ_{-6}:	0	-1.66	0	0	1.07	0

$$\tag{5.11}$$

where the matrix elements $\int\psi_i^* V_\perp \psi_{-i} d\tau$ are the same as $\int\psi_{-i}^* V_\perp \psi_i d\tau$ and where all other elements are zero.

In evaluating these elements we have not yet included the small correction for the second-order admixture of $^4T_2(^4F)$ into the $^4T_1(^4F)$ term by the spin-orbit coupling. For our purpose it will suffice to include the correction only in the diagonal elements between the states of the ground Kramers doublet, since these elements produce the dominant contribution to susceptibility in the region of temperature with which we shall be concerned. Including this small correction, the modified matrix elements are

$$\int\psi_{\pm1}^* V_{||}\psi_{\pm1}d\tau = 1.695 \quad \text{and} \quad \int\psi_{\pm1}^* V_\perp\psi_{\mp1}d\tau = 2.415.$$

The perturbed energy levels, to the second order in H_0, may now be calculated and are

(a) for H_0 parallel to c_0

$$E_{\pm 1} = 3.88\lambda' \pm 1.695\beta H_0 + \frac{1.89}{\lambda'}\beta^2 H_0^2$$

$$E_{\pm 2} = 2.11\lambda' \pm 2.25\beta H_0 + \frac{0.44}{\lambda'}\beta^2 H_0^2$$

$$E_{\pm 3} = 1.06\lambda' \pm 1.55\beta H_0 - \frac{0.20}{\lambda'}\beta^2 H_0^2$$

$$E_{\pm 4} = -1.93\lambda' \mp 0.10\beta H_0 - \frac{1.69}{\lambda'}\beta^2 H_0^2$$

$$E_{\pm 5} = -2.30\lambda' \pm 0.39\beta H_0 - \frac{0.44}{\lambda'}\beta^2 H_0^2$$

$$E_{\pm 6} = -2.81\lambda' \pm 1.65\beta H_0$$

(b) for H_0 perpendicular to c_0

$$E_{\pm 1} = 3.88\lambda' \pm 2.415\beta H_0 + \frac{3.28}{\lambda'}\beta^2 H_0^2$$

$$E_{\pm 2} = 2.11\lambda' - \frac{2.07}{\lambda'}\beta^2 H_0^2$$

$$E_{\pm 3} = 1.06\lambda' \mp 1.14\beta H_0 + \frac{0.43}{\lambda'}\beta^2 H_0^2$$

$$E_{\pm 4} = -1.93\lambda' \pm 0.82\beta H_0 + \frac{2.27}{\lambda'}\beta^2 H_0^2$$

$$E_{\pm 5} = -2.30\lambda' - \frac{1.10}{\lambda'}\beta^2 H_0^2$$

$$E_{\pm 6} = -2.81\lambda' - \frac{2.81}{\lambda'}\beta^2 H_0^2. \tag{5.12}$$

If, in general, we write $E_i = W_i + W_i'H_0 + W_i''H_0^2$, then the magnetic susceptibility (see Van Vleck[22]) is given by

$$\chi = \frac{\sum_i N[(W_i'^2/kT) - 2W_i'']\exp(-W_i/kT)}{\sum_i \exp(-W_i/kT)}. \tag{5.13}$$

It follows from the Eq. (5.12) that, for our case,

$$\chi_{\shortparallel} = N\beta^2[(A_{\shortparallel}/kT) + (B_{\shortparallel}/\lambda')], \tag{5.14}$$

$$\chi_\perp = N\beta^2[(A_\perp/kT) + (B_\perp/\lambda')], \tag{5.15}$$

where the quantities $A_{\shortparallel}$, $A_\perp$, $B_{\shortparallel}$, $B_\perp$, are shown graphically as functions of λ'/kT in Fig. 3.

We may now introduce the exchange interactions, and we shall do so in the molecular-field approximation. A difficulty which arises immediately concerns the fact that the values deduced in Sec. 3 for the exchange parameters in CoCl₂ apply only to that region of temperature for which all ions, to a good approximation, are in the ground doublet, whereas we now wish to consider temperatures well outside this region. As the ions populate the higher levels, so we may expect the exchange interactions to change. In this work, we shall be forced to make the approximation that the exchange parameters are temperature-independent, having the values deduced in Sec. 3. As far as susceptibility is concerned, this approximation should be quite good, since the cooperative effects are most important in the lower temperature regions where the exchange parameters will be close to the values we assume. At high temperatures, the cooperative effect is small and the

[22] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

susceptibility is largely insensitive to the exchange parameters.

In the complete absence of cooperative effects, the susceptibility can be thought of as being produced by a single "effective" temperature-dependent Kramers doublet with energy

$$E_\pm = W \pm W'H_0 + W''H_0^2, \tag{5.16}$$

where

$$W' = \beta\sqrt{A}, \quad \text{and} \quad W'' = -\beta^2 B/2\lambda' \tag{5.17}$$

and where here and henceforth $A = A_{\shortparallel}$, $B = B_{\shortparallel}$, when H_0 is parallel to c_0, and $A = A_\perp$, $B = B_\perp$, when H_0 is perpendicular to c_0.

Let us now introduce the two sublattices "a" and "b," together with the molecular fields H_{ia} and H_{ib} acting, respectively, upon the "a" and "b" sublattices. We have [compare (5.16)], including the internal fields

$$E_a = W \pm W'H_a + W''H_0^2,$$
$$E_b = W \pm W'H_b + W''H_0^2, \tag{5.18}$$

where

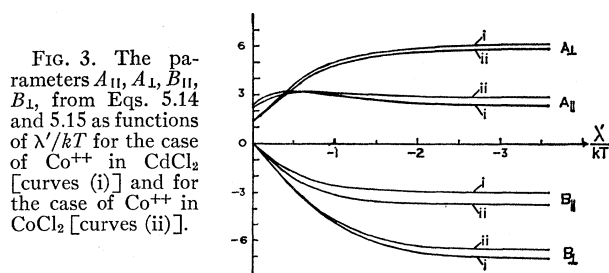$$H_a = H_0 + H_{ia}, \quad \text{and} \quad H_b = H_0 + H_{ib}. \tag{5.19}$$

FIG. 3. The parameters $A_{\shortparallel}$, $A_\perp$, $B_{\shortparallel}$, $B_\perp$, from Eqs. 5.14 and 5.15 as functions of λ'/kT for the case of Co⁺⁺ in CdCl₂ [curves (i)] and for the case of Co⁺⁺ in CoCl₂ [curves (ii)].
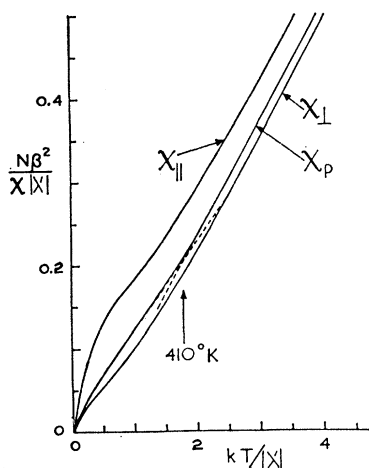
FIG. 4. The inverse molar susceptibility plotted as a function of temperature for the case of Co^{++} in $CdCl_2$ showing the two linear regions of the powder susceptibility curve (χ_p) where a Curie-Weiss law is obeyed.

From Eqs. (5.3) and (5.4) we find

$$H_{ia} = -\frac{6}{g\beta}[J_2\bar{s}_b - J_1\bar{s}_a + \sigma(D_1\bar{s}_a - D_2\bar{s}_b)],$$

$$\tag{5.20}$$

$$H_{ib} = -\frac{6}{g\beta}[J_2\bar{s}_a - J_1\bar{s}_b + \sigma(D_1\bar{s}_b - D_2\bar{s}_a)],$$

where $\sigma = 0$ when H_0 is perpendicular to c_0, and $\sigma = 1$ when H_0 is parallel to c_0, and where $g = 2\sqrt{A}$.

The magnetic moment of an "a" site ion and of a "b" site ion are, respectively,

$$m_a = -\partial E_a/\partial H_0 = \mp W' - 2W''H_0,$$
$$m_b = -\partial E_b/\partial H_0 = \mp W' - 2W''H_0.$$
$$\tag{5.21}$$

The average values of magnetic moment upon each sublattice site are, therefore,

$$\bar{m}_a = \frac{\sum m_a \exp(-E_a/kT)}{\sum \exp(-E_a/kT)}$$

and

$$\bar{m}_b = \frac{\sum m_b \exp(-E_b/kT)}{\sum \exp(-E_b/kT)},$$
$$\tag{5.22}$$

the summations being taken over the two states of the "fictitious" ground doublet. Expanding the exponentials, and retaining only terms to first order in H_0, H_a, and H_b, we find

$$\bar{m}_a + \bar{m}_b = [(W')^2/kT](H_a + H_b) - 4W''H_0. \quad (5.23)$$

Using (5.17), (5.19), and (5.20), we now find for the molar susceptibility

$$\chi = \frac{4N\beta^2 kT[(A/kT) + (B/\lambda')]}{4kT + 6[J_2 - J_1 + \sigma(D_1 - D_2)]}. \quad (5.24)$$

Using the values of A and B obtained from Fig. 3, we may now plot the high-temperature susceptibility as a

function of temperature provided that we first estimate the magnitude of λ'.

Work by other authors upon cobalt salts (see, for example, Low[16] and Bose, Chakravarty and Chatterjee[23] seems to favor a value for λ which is either very close to, or slightly reduced from the value -180 cm^{-1}. In this paper, however, we shall make an independent estimate as follows. For very small concentrations of Co^{++} in $CdCl_2$, we have earlier deduced a value for the ratio of trigonal distortion to spin-orbit coupling (see Fig. 1). This fixes the relative energies of the six ground Kramers doublets and we may, therefore, estimate the constants A and B of Eqs. (5.14) and (5.15) for this case, exactly as we did for $CoCl_2$. These parameters (for Co^{++} in $CdCl_2$) are shown in Fig. 3. For small concentrations of cobalt in the $CdCl_2$ lattice we may evaluate the parallel and perpendicular susceptibilities directly from (5.14) and (5.15) since the cooperative effects will be negligible. These equations may be written

$$-N\beta^2/\chi\lambda' = 1/(Ay - B), \quad (5.25)$$

where $y = -\lambda'/kT$. We may, therefore, plot $N\beta^2/\chi|\lambda'|$ against $1/y$ and this is done in Fig. 4.

Experimental work on susceptibility using salts containing varying concentrations of cobalt in $CdCl_2$ has been performed by Fehrenbach.[24] He reports that the powder susceptibility (after correction for diamagnetic contributions from the host lattice) follows a Curie-Weiss law of the form $C/(T-\Theta)$, but that for each concentration investigated, the constants of this equation suddenly change their values in the region $T \doteq 410°$K. The values of the constants are, of course, different for each concentration, but the temperature of the anomaly is almost independent of concentration.

The powder susceptibility χ_p is obtained from the susceptibilities parallel and perpendicular to c_0 by the
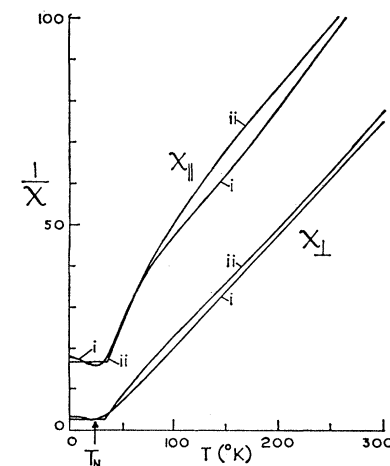

FIG. 5. A plot of the inverse molar susceptibility for $CoCl_2$ (both parallel and perpendicular to the hexagonal axis) as a function of temperature, comparing the theoretical curves (ii) with the experimental results (i) as measured by Bizette et al. (Ref. 3).

[23] A. Bose, A. S. Chakravarty, and R. Chatterjee, Proc. Roy. Soc. (London) A261, 43 (1961).

equation

$$\chi_p = \tfrac{1}{3}(\chi_{||} + 2\chi_\perp), \qquad (5.26)$$

and this curve is also drawn in Fig. 4. We see that the theory does, indeed, indicate a change in the slope, albeit, not quite so sharp as that seen by Fehrenbach.[24] For $0.3 < 1/y < 1.6$ the powder curve does follow to a good approximation a Curie-Weiss law (with negative Θ). Also, for $1/y > 2.2$ the curve also obeys a Curie-Weiss law, but now with positive Θ. If we extend these two linear regions we may equate the value of T at the point of intersection with the temperature ($\doteq 410°$K) which Fehrenbach finds for the sudden change of slope.

[24] C. Fehrenbach, J. Phys. Radium 8, 11 (1937).

The required point is

$$1/y = -kT/\lambda' = 1.80,$$

which gives $\lambda' = -158$ cm^{-1} or, taking $k = 0.9$, a value of $\lambda = -176$ cm^{-1}.

Using this value for the spin orbit coupling constant in CoCl$_2$ (assuming, therefore, that this quantity has approximately the same value for CoCl$_2$ as for Co^{++} in CdCl$_2$) we may now evaluate $1/\chi$ as a function of temperature for the concentrated salt. The results are shown in Fig. 5 together with the experimental curves of Bizette et al.[3] We see that the agreement between theory and experiment is quite good for both $\chi_{||}$ and $\chi_\perp$.

Structure of the F Center in NaF†

WILLIAM T. DOYLE

Physics Department, Dartmouth College, Hanover, New Hampshire

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The electron-nuclear double resonance (ENDOR) method is applied to the study of the structure of the F center in NaF. Hyperfine interactions between the F-center electron and a number of the surrounding nuclear shells are presented and compared with the results of earlier experiments and with theory. It is found that the resolved hyperfine structure is not due to the predominance of the first-shell interaction, as has been thought, but it arises from the fortuitous equality of the first- and second-shell isotropic hyperfine interactions. Electron paramagnetic resonance (EPR) absorption measurements of the resolved structure confirms an expected 31-line resolved pattern. The exceptional resolution found in the ENDOR spectrum permits the identification of interactions with nuclei well beyond the eighth shell. Although the samples also contained large numbers of M centers, no evidence for a paramagnetic M center was found in either the EPR or ENDOR spectra.

I. INTRODUCTION

THE shape of electron paramagnetic resonance (EPR) lines due to F centers in alkali halide crystals arises from hyperfine interactions between the F-center electron and the surrounding nuclei.[1] Although F centers typically exhibit a single broad Gaussian EPR line, in a few crystals, viz., LiF,[2,3] NaF,[2,3] NaH,[4] RbCl,[5] and CsCl,[6] a resolved spectrum has been observed. Rather special relations must obtain among the hyperfine interactions for a resolved spectrum to appear. The simplest case arises when the isotropic interaction with the first shell predominates. Then, if the spin of the first-shell nuclei is $\tfrac{3}{2}$, one expects a nineteen-line

spectrum with a distribution of intensities of 1, 6, 21, 56, 120, 216, 336, 456, 546, and 580, corresponding to total shell nuclear magnetic quantum numbers of ± 9, $\cdots$, 0, respectively.[1] This simple nineteen-line spectrum has been reported in LiF,[2,3] NaF,[2–4,7] and NaH.[4,8] In LiF, however, it is now known that the resolved structure is considerably more complicated. Many more than nineteen lines are observed and the pattern depends strongly upon the orientation of the crystal in the external magnetic field.[7,9,10] In some crystal orientations,[9] and in powdered samples,[4] the resolved structure is obliterated. Electron-nuclear double resonance (ENDOR)[11] studies have shown that in LiF the resolved structure is due to both isotropic and anisotropic hyperfine interactions with the first two nuclear shells[7,10,12]; interactions with all other shells being small

[1] A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, Phys. Rev. 91, 1066 (1953).
[2] N. Lord, Phys. Rev. 105, 756 (1957).
[3] G. J. Wolga and M. W. P. Strandberg, J. Phys. Chem. Solids 9, 309 (1959).
[4] W. T. Doyle and W. L. Williams, Phys. Rev. Letters 6, 537 (1961).
[5] H. C. Wolf and K. H. Hausser, Naturwissenschaften 46, 646 (1959).
[6] F. H. Hughes and J. G. Allard, Phys. Rev. 125, 173 (1962).

[7] W. C. Holton and H. Blum, Phys. Rev. 125, 89 (1962).
[8] W. L. Williams, Phys. Rev. 125, 82 (1962).
[9] Y. W. Kim, R. Kaplan, and P. J. Bray, Phys. Rev. Letters 6, 4 (1961).
[10] W. C. Holton, H. Blum, and C. P. Slichter, Phys. Rev. Letters 5, 197 (1960).
[11] G. Feher, Phys. Rev. 105, 1122 (1957).
[12] N. Lord, Phys. Rev. Letters 1, 170 (1958).