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Influence of Crystalline Fields on the Susceptibilities of Salts of Paramagnetic Ions. II. The Iron Group, Especially Ni, Cr and Co

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The present paper is concerned with the calculation of the paramagnetic susceptibility of highly hydrated crystals of the iron group elements Ni, Cr and Co. On the assumption that the metallic ion is subject to a crystalline electric field, predominantly cubic but also with a smaller rhombic term, the Hamiltonian function in a magnetic field $\boldsymbol{H}$ is given by

$$D(x^4+y^4+z^4)+Ax^2+By^2-(A+B)z^2+\lambda(\boldsymbol{L}\cdot\boldsymbol{S})+\beta\boldsymbol{H}\cdot(\boldsymbol{L}+2\boldsymbol{S})$$

the numerical value of λ being known from the work of Laporte but the other constants yet to be determined. It actually proves possible to formulate and solve approximately the resulting secular equations and so obtain the first and second order Zeeman effects and hence the susceptibility. For all three ions $L=3$, so that the orbital problem is the same for all. This problem is exactly soluble, the energy levels consisting of two triplets and a singlet, the singlet not lying between the triplets. The effect of the introduction of the spin and its coupling to the orbit then leads to a determinant of order 21 for Ni and of order 28 for Cr and Co. That for Ni factors into one of order 10 and one of order 11, while those for Cr and Co factor into two determinants, identical except for the sign of the coefficient of H. On the assumption of a cubic field of the same sign and of approximately the same magnitude for all three ions the orbit-spin, together with the rhombic field, is able to remove the degeneracy of the lowest level in Ni and Cr only in a high approximation, while with Co the degeneracy is removed in first approximation. This difference accounts for the isotropy of Ni and Cr compared with the anisotropy of Co. In order to obtain agreement with experiment it is necessary to assume that in Ni the singlet of the orbital problem lies lowest. It then follows from the work of Van Vleck that the singlet also lies lowest for Cr but that for Co the singlet lies highest. When the singlet lies lowest, the square of the magneton number is given by the "spin only" value $4S(S+1)$, together with a small orbital contribution of order λ/D, whose sign can be either positive or negative. Actually it is positive for Ni and negative for Cr. In order to fit the results on the principal susceptibilities of Ni, it is necessary to take $D=1260$ cm^{-1}, $A=176$ cm^{-1}, $B=352$ cm^{-1}, the magnitude of λ being -335 cm^{-1}. For Ni and Cr the theory requires that for the mean susceptibility $\chi=Q+P/T$, where P and Q are constants, Q being uniquely determined when P is fixed. Choosing P so that χT passes through the experimental point at 170°K we find that good agreement is obtained over the whole temperature range. For Cr $\lambda=87$ cm^{-1} and we find $D=3730$ cm^{-1}, but we cannot determine A or B since there are no data on the principal susceptibilities.

Computational difficulties prevent the accurate solution of the Co problem. The situation is complicated by the experimental data not being complete. It proves necessary to consider a sextet which is soluble only numerically in the general case but perturbation theory can be applied when either the orbit-spin is large compared with the rhombic field or *vice-versa*. We obtain fair agreement with experiment and our calculations indicate that good agreement would be obtained in an intermediate case.

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INTRODUCTION

IN THE following paper the idea of crystal fields of definite symmetry, developed by Van Vleck and others,[1] and already used in a previous article by the authors,[2] is applied to calculate the susceptibilities of salts of the elements Ni, Co and Cr. There are two respects in which the present problem differs from that of susceptibilities in the rare earth group. In the first place, the incomplete shell which is responsible for the paramagnetism of the iron elements consists of *3d* electrons, which are much more strongly affected by the crystal fields than the more sheltered *4f* shell of the rare earths. In the second place the orbit-spin coupling, which determines the multiplet width, is usually smaller in the iron group than in the rare earths. For the latter it was allowable to suppose that each multiplet component underwent a "Stark effect" due to the crystal field, without distortion on account of the other multiplet components. In the iron group, however, the electric field of the crystal is able to break down the relatively weak coupling between orbit and spin, producing an electric Paschen-Back effect; the orbit-spin coupling may be treated hence as a perturbation on an unperturbed problem which neglects the spin. This unperturbed, or orbital problem, as we shall call it, is the same for all three ions Ni^{++} Co^{++} Cr^{++}, since they all have an F state ($L=3$) as ground state.

We assume that the crystal field has no more than rhombic symmetry.[3] The high degree of isotropy of Ni salts suggests that in this case the departure from cubic symmetry is small. Now it is known that a field which is nearly cubic decomposes the seven coincident levels of the F state (without spin) into a single level and two triplets, the single level lying outside the triplets and the triplet widths being small compared with the singlet-triplet or the triplet-triplet separations. If the spin and its coupling to the orbit be included, further decompositions of these levels occur. The general theory of susceptibilities shows that Curie's law will cease to be obeyed at low temperatures if kT becomes comparable with the separation of the lowest group of levels. The close conformity of Ni salts to Curie's law over a range of temperature from 300°K down to 14°K thus requires that a very narrow group of levels must lie considerably below all others. These conditions are satisfied if the single level of the orbital problem lies below the others, and on this assumption it is possible to account qualitatively for both the small anisotropy and the conformity to Curie's law. This arrangement of levels, however, appears to preclude an explanation on the same lines of the much greater anisotropy of the very similar and sometimes isomorphous salts of Co, and of the considerable departures from Curie's law which they exhibit. To ac-

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[1] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford (1932).

[2] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932). Attention may be called here to a printers error in this paper. Minus signs were omitted in Eqs. (8) and (9) which should read $q=-I/10395$ for (8) and $q=-I/32670$ for (9). Moreover, in the secular determinant for *Pr* $a=\frac{1}{2}pD$ (not pD) and similarly for *Nd* $A=6ap(14)^{1/2}$.

[3] The assumption of a rhombic field not predominantly cubic was found to lead to very large asymmetry, in contradiction with experiment.

count for the behavior of Co salts it is necessary to suppose that the levels of the orbital problem in Co are inverted relatively to those in Ni. That such an inversion is actually to be expected in passing from Ni and Cr to Co has been neatly demonstrated by Van Vleck.[4]

Experimental Data

It is useful at this stage to review the experimental data available on the hydrated salts of Ni, Cr and Co. We restrict ourselves to salts of large magnetic dilution, so that exchange effects may be neglected. Determinations of the three principal susceptibilities of the double sulphates of Co with ammonium, potassium and rubidium, have been made by Rabi[5] at 300°K. Jackson[6] has measured the susceptibility of powdered $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and Gorter, de Haas and v. d. Handel[7] that of powdered $NiSO_4 \cdot 7H_2O$ over a range of temperature between 14°K and 290°K. The graph of $1/\chi$ against T is approximately a straight line through the origin in both cases. Jackson[6] has measured the three principal susceptibilities of $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$ at various temperatures down to 14°K. His values of the susceptibility extrapolated to a temperature of 300°K differ considerably from Rabi's, and there is only one determination between 20° and 290°K. As far as one can judge, however, the graph of $1/\chi$ against T is a straight line for each of the three principal susceptibilities, down to a temperature of about 50°K, below which the curve bends downwards slightly, so that the susceptibilities are higher than those predicted by the relation $\chi = C/(T+\Delta)$ of Weiss.

Very recently determinations over a temperature range from 250°K to 360°K have been made by Bartlett[8] for crystalline cobalt ammonium sulphate and certain other crystals. They seem to be the most reliable measurements yet taken, being consistent and in agreement with Rabi's at the single temperature used by him. We are indebted to Dr. Bartlett for communicating these results to us in advance of publication.

The susceptibility of potassium chrome alum in powder form has been measured by de Haas and Gorter[9] at various temperatures between 290°K and 14°K. They find that the law $\chi = C/T$ is closely obeyed over the whole range. Chrome alum forms crystals in the cubic system so that it may be expected to be magnetically isotropic.[10]

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[4] J. H. Van Vleck, Phys. Rev. **41**, 208 (1932).

[5] I. I. Rabi, Phys. Rev. **29**, 184 (1927).

[6] L. C. Jackson, Phil. Trans. Roy. Soc. London, **224**, 1 (1922), Leiden Com. 163.

[7] C. J. Gorter, W. J. de Haas and v. d. Handel, Proc. Amst. Acad. **34**, 1 (1931), Leiden Com. 218d.

[8] B. W. Bartlett, Phys. Rev. **41**, 818 (1932).

[9] W. J. de Haas and C. J. Gorter, Leiden Com. 208d.

[10] Measurements of the susceptibilities of the paramagnetic cubic crystal pyrite were made long ago by Voigt and Kinoshita (Ann. d. Physik **24**, 492 (1907)) who found it to be magnetically isotropic. There does not, however, seem to be any reason why magnetic dissymmetry should not exist in cubic crystals, as the electric field acting on the ion may have a lower symmetry than the lattice. See also reference **18**.

THE ION IN A PERFECTLY CUBIC FIELD

Before considering the secular determinant explicitly, it is instructive to look at the problem from a more general point of view. The analysis of Bethe[11] shows that the cubic field breaks up the F level into three, corresponding to the irreducible representations Γ_2, Γ_4, Γ_5, of the cubic group, in his notation. The level Γ_5 lies between Γ_2 and Γ_4; Γ_2 is single, while Γ_4 and Γ_5 are each triply degenerate. We shall see later that the intervals between Γ_2, Γ_4, Γ_5 are of the order 10^4 cm^{-1}. The reader is referred to Van Vleck's[4] paper for the demonstration of the fact that in Ni and Cr Γ_2 lies lowest and in Co Γ_4 lies lowest, for a given sign of D in the Hamiltonian. The level Γ_2 is non-magnetic; that is to say an atom in this state has no average orbital magnetic moment. The level Γ_4 is magnetic. Hence if Γ_2 is lowest the orbit is "quenched", i.e., contributes nothing to the susceptibility except a term independent of temperature. If, however, Γ_4 is lowest a certain portion survives.

We have now to consider the influence of the spin. Inclusion of the spin S $(=1$ for Ni and $3/2$ for Co and Cr) without interaction with the orbit makes each level of the orbital problem have an additional $(2S+1)$-fold degeneracy, which is partially removed by the interaction. By the methods of Bethe's paper the decomposition of the levels is found by reducing the six direct products $\Gamma_i D_k$, $(i=2,\ 4,\ 5;\ k=1,\ 3/2)$ to represent the cubic group. Here D_k is the representation group for the rotation of the spin k alone. The result is, in Bethe's notation,

$$\begin{aligned} \Gamma_2 D_1 &= \Gamma_5, & \Gamma_2 D_{3/2} &= \Gamma_8 \\ \Gamma_4 D_1 &= \Gamma_2+\Gamma_3+\Gamma_4+\Gamma_5, & \Gamma_4 D_{3/2} &= \Gamma_6+\Gamma_7+2\Gamma_8, \\ \Gamma_5 D_1 &= \Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5, & \Gamma_5 D_{3/2} &= \Gamma_6+\Gamma_7+2\Gamma_8. \end{aligned} \tag{1}$$

Here Γ_6, Γ_7, Γ_8 are the "zweideutig" representations of the cubic group, of dimensions 2, 2, 4, respectively, which always arise with half-integral quantum numbers. These equations state that for Ni, Cr and Co the orbit-spin-interaction does not split the cubic level Γ_2 but splits each of the levels Γ_4, Γ_5 into four components.

Let us suppose that the level Γ_2 of the orbital problem lies lowest. The above reductions show that under the orbit-spin interaction this level does not break up, but remains triply degenerate (in Ni) or quadruply degenerate (in Co and Cr); no energy differences arise in consequence of different orientations of the spin, which therefore remains entirely free at all temperatures to orientate itself along the magnetic field. If the orbital contribution to the moment be neglected, the magneton number would be the Bose-Stoner or "spin only" value $[4S(S+1)]^{1/2}$. A further deduction is that the orbit-spin interaction causes the state Γ_2 to interact with components of Γ_4 and Γ_5 as is seen from the threefold occurrence of Γ_5 or Γ_8 on the right-hand side of (1). This produces a sharing of properties, and in particular gives rise to an orbital contribution to the magnetic moment in the state Γ_2 which is of order

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[11] H. Bethe, Ann. d. Physik **3**, 133 (1929).

λ/D. Thus the orbit-spin coupling produces, in an ion in a cubic field, departures from the Bose-Stoner value which may be either positive or negative according to the sign of λ/D.

The circumstances are not quite so simple if the state Γ_4 lies lowest. Here the orbit-spin coupling partially removes the degeneracy, so that different orientations of the spin have different energies, although, of course, it is not possible to associate a definite axial quantization of the spin with each of the levels. Thus the spin is only partially free and the orbital contribution will also be modified.

THE CONSTANT Δ

In a cubic field the quantity Δ of the Curie-Weiss formula $\chi = C/(T+\Delta)$ is given to a first approximation by the ratio of the coefficients of $1/T$ and $1/T^2$ in the expansion of the susceptibility in inverse powers of T. If we make the usual assumption that the magnetic moment in the absence of the magnetic field contains, besides low-frequency elements $M(n,\ n')$, only high-frequency elements, and none of intermediate frequency, it is easily shown[12] that

$$k\Delta = \left\{ \sum_{nn'} W_n \,|\, M(n,\ n') \,|\,^2 / \sum |\, M(n,\ n') \,|\,^2 \right\} - \overline{W}$$

the summation being over the group of levels connected by low-frequency elements, and $\overline{W}$ being their mean energy. When the level Γ_2 of the orbital problem, which is not split up by the orbit-spin interaction, lies lowest, the magnetic mean center and the energetic mean center, whose difference gives $k\Delta$ according to the last equation, necessarily coincide. Hence in this case the susceptibility is of the form $\chi = C/T$, correct to terms in $1/T^2$. To this approximation the ion in a cubic field behaves as if it were in the gaseous state.

If the level Γ_4 lies lowest, the magnetic mean center and the energetic mean center do not necessarily coincide, so that the susceptibility will in general have a term in $1/T^2$. Thus leaving aside the question of asymmetry produced by a rhombic field, which is considered in the next section, we should expect Ni and Cr to conform much more closely to Curie's law than Co, as is indeed found to be the case.

ASYMMETRY DUE TO A RHOMBIC FIELD

Let us for the moment neglect the spin. The effect of superposing a rhombic field on the cubic field is, as shown by Bethe,[11] to remove all the degeneracy in the orbital problem, the appropriate reduction being

$$\Gamma_2 = G_1,\ \Gamma_4 = G_2 + G_3 + G_4,\ \Gamma_5 = G_2 + G_3 + G_4, \qquad (2)$$

where G_1, G_2, G_3, G_4 are the four one-dimensional representations of the rhombic group. Fig. 1 shows diagrammatically the decomposition of the levels under the various fields. The level Γ_2 is seen to be completely isolated

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[12] C. J. Gorter, Arch. Musee Teyler, 7 (3), 183 (1932). This formula can readily be obtained from the equation for $k\Delta$ on page 197, reference 2, $\overline{W}$ in this case having been chosen to be zero.

from the others. The rhombic field alone, unlike the orbit-spin coupling, does not lead to a sharing of properties between Γ_2 and the other states. If Γ_2 is lowest the rhombic field does not give rise to any orbital contribution to the part of the susceptibility depending on the temperature. The part independent of the temperature is rendered slightly asymmetrical. Although no asymmetry is introduced directly by the rhombic field, the orbit-spin interaction, as we have seen, evokes an orbital contribution to the susceptibility, and this will be rendered anisotropic by the rhombic field. The anisotropy is thus a second order effect; the rhombic field may be comparatively large without producing much anisotropy. Neither the rhombic field alone nor the orbit-spin interaction alone can split the level Γ_2 of the cubic field. Both acting together will remove all degeneracy, but the separation produced will depend on a cross term and in addition is a second order effect in λ owing to the vanishing of the mean orbital angular momentum. If the level Γ_4 is lowest, these conclusions do not hold, both the anisotropy and Δ being first order effects of the rhombic field.

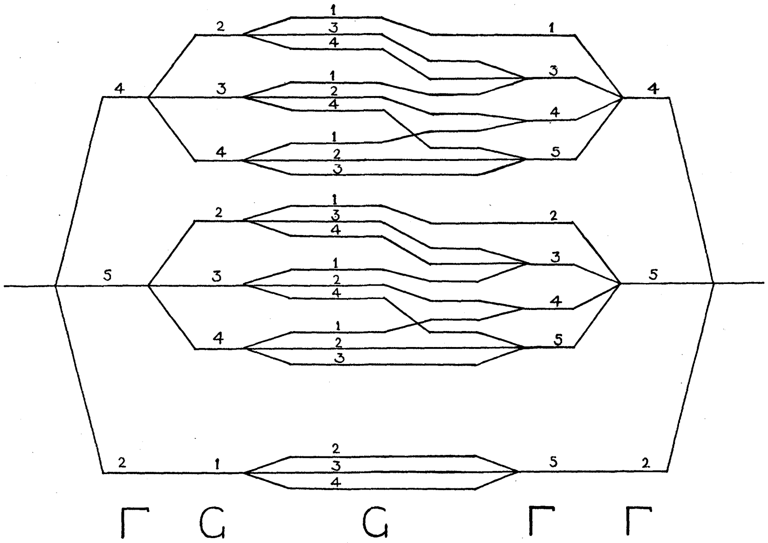

Fig. 1. Fig. 1 shows how the ^3F state in nickel is affected by the cubic field, the rhombic field and the orbit-spin coupling. By starting at the left with the free ion, the cubic field splits the single level into three, the numbers and symbols underneath denoting to which representation, in Bethe's notation, the levels belong. The application of the rhombic field splits Γ_4 and Γ_5 each into three, leaving Γ_2 single. The addition of the orbit-spin then removes all the remaining degeneracy. Making the rhombic field zero leaves only orbit-spin and cubic, the way the levels come together being shown. Removal of the orbit-spin leaves only the cubic field, and making this shrink to zero gives once again the free ion.

If Γ_2 lies lowest, as in Ni and Cr, it is possible to prove a result very similar to that which was shown to hold for the rare earths, namely that the expansion of χ for a crystal powder should contain no term in $1/T^2$. The Hamiltonian inclusive of the magnetic field is invariant for a half turn about the magnetic field. The group consisting of this operation and the identical operation has two one-dimensional (eindeutig) representations, associated respectively with the odd and even series of values of the quantum number M. (M is not a good quantum number when the electric field and $(\boldsymbol{L}\cdot\boldsymbol{S})$ are diagonalized.) It is clear that of the three constituent levels ϵ_1, ϵ_2, ϵ_3 of Γ_2, two, (ϵ_1, ϵ_2) belong to one representation, and the third (ϵ_3) to the other. The third level has therefore no magnetic or other connection with the other two, which are linked to each other. In the presence of the magnetic field, the level ϵ_3 is unaltered, while ϵ_1, ϵ_2 undergo equal and opposite displacements away from each other. This neglects the high-frequency shift, which is practically the same for all three levels. The value of $k\Delta$ is therefore $(\epsilon_1+\epsilon_2+\epsilon_3)/3-(\epsilon_1+\epsilon_2)/2=(2\epsilon_3-\epsilon_1-\epsilon_2)/6$, an expression which is of course invariant of the origin of energy. On permuting the axes the "field free" levels ϵ_1, ϵ_2, ϵ_3 undergo a corresponding permutation; if we average the above expressions for $k\Delta$ over three cyclic permutations, which corresponds to finding the value of $k\Delta$ for a crystal powder, the result is seen to vanish.

We now turn our attention to the secular determinant of the problem in order to give the considerations of the foregoing sections a more quantitative form.

THE SECULAR DETERMINANT

The Hamiltonian

We assume a Hamiltonian function

$$\sum_i [D(x_i^4 + y_i^4 + z_i^4) + Ax_i^2 + By_i^2 - (A + B)z_i^2] + \lambda(\boldsymbol{L}\cdot\boldsymbol{S}) + \beta\boldsymbol{H}\cdot(\boldsymbol{L} + 2\boldsymbol{S}) \quad (3)$$

where A, B, D are constants specifying the crystal field, λ is the constant of the orbit-spin interaction, β is the Bohr magneton $eh/4\pi mc$ and $\boldsymbol{H}$ is the magnetic field.

In the Hamiltonian (3) the dominant term is the term in D. The most general field of rhombic symmetry which is nearly cubic would give a Hamiltonian containing other terms in addition to those written down. These would be of higher order and no greater generality would be obtained by their inclusion. The rhombic term and the orbit-spin coupling are of comparable magnitude. The magnetic energy may always be regarded as a small perturbation in calculating the susceptibility, even though the field is strong enough to produce a Paschen-Back effect, always provided that the magnetic separations do not become comparable with kT so that saturation effects occur. This follows from an application of the principle of spectroscopic stability due to Van Vleck.[13]

The matrix elements

The following matrix elements in the (M_L, M_S) system of quantization are required. They have been obtained by the method used in the previous paper.[2]

$$D\sum_i (x_i^4 + y_i^4 + z_i^4)(M_L, M_L)$$
$$= \text{const.} + q'DM_L^2[7M_L^2 + 5 - 6L(L + 1)],$$
$$D\sum (x_i^4 + y_i^4 + z_i^4)(M_L, M_L \pm 4)$$
$$= \tfrac{1}{2}q'D[(L \mp M_L)!(L \pm M_L + 4)!/(L \pm M_L)!(L \mp M_L - 4)!]^{1/2},$$

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[13] Reference 1, page 231.

$$\begin{aligned}
&\sum[Ax_i^2+By_i^2-(A+B)z_i^2](M_L,\,M_L)\\
&\quad=\text{const.}+\tfrac{1}{2}a(A+B)[3M_L^2-L(L+1)],\\
&\sum[Ax_i^2+By_i^2-(A+B)z_i^2](M_L,\,M_L\pm 2)\\
&\quad=-a(A-B)[(L\mp M_L)!(L\pm M_L+2)!/(L\mp M_L-2)!(L\pm M_L)!]^{1/2}/4.
\end{aligned}$$

Here q and a are the ratios of the matrix elements calculated for a system of n electrons to those for a one-electron system; the sign of q has been discussed by Van Vleck.[4] The summation is over all the electrons of the incomplete group. The two additive constants, as well as q and a, are independent of M_L. These matrix elements are all diagonal in L. The elements non-diagonal in L are not required, since the crystal field is assumed not to destroy the Russell-Saunders coupling of the vectors $\boldsymbol{l}_i$, $\boldsymbol{s}_i$. Since the elements do not involve the spin, they may be regarded as diagonal in M_S. We also require

$$(\boldsymbol{L}\cdot\boldsymbol{S})(M_L,\,M_S;\,M_L,\,M_S)=M_LM_S,$$

$$\begin{aligned}
&(\boldsymbol{L}\cdot\boldsymbol{S})(M_L,\,M_S;\,M_L\pm 1,\,M_S\mp 1)\\
&\qquad=\tfrac{1}{2}[(S\pm M_S)(S\mp M_S+1)(L\mp M_L)(L\pm M_L+1)]^{1/2}.
\end{aligned}$$

The secular determinant

The orbital problem, being common to all three ions Ni, Co, Cr, may be treated first. The orbital terms of the Hamiltonian are all of type $\Delta M_L=0$, ± 2, ± 4, so that the secular determinant

$$\mathcal{H}(M_L,\,M_S;\,M_L',\,M_S')-\delta(M_L,\,M_S;\,M_L',\,M_S')W=0,$$

breaks up into two factors, one of the fourth order involving $M_L=\pm 3$, ± 1, and one of the third order involving $M_L=0$, ± 2. These factors are symmetrical about the principal and secondary diagonals, so that it is necessary to write down only the first row and central elements of the second row of each

$$\left|\begin{array}{cccc} -3Dq+15\sigma & -15^{1/2}\delta & 15^{1/2}Dq & 0\\ & -5Dq-9\sigma & -6\delta & \end{array}\right|,\quad \left|\begin{array}{ccc} -13Dq & -30^{1/2}\delta & 5Dq\\ & -12\sigma & \end{array}\right|$$

Here σ, δ have been written for $a(A\pm B)/2$ and $q=12q'$. The terms in D can be diagonalized[14] by means of unitary transformations SS^{-1}, TT^{-1} with

$$S=(\tfrac{1}{4})\begin{pmatrix} h & k & -k & -h\\ -k & h & -h & k\\ k & h & h & k\\ h & -k & -k & h \end{pmatrix}\quad \begin{aligned} h&=5^{1/2}\\ k&=3^{1/2}\end{aligned}\quad T=(\tfrac{1}{2})^{1/2}\begin{pmatrix} 1 & 0 & 1\\ 0 & 2^{1/2} & 0\\ -1 & 0 & 1 \end{pmatrix}$$

We may denote the matrices S, T by $S(N,\,M_L)$, $T(N,\,M_L)$. The columns are numbered by M_L having values -3, -1, 1, 3, for S and -2, 0, 2 for T. The

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[14] The wave functions $S\psi$, $T\psi$ which the transformations S, T introduce are precisely those given by Bethe (reference 11, page 166). They diagonalize the cubic and rhombic fields except for matrix elements of the rhombic field between different cubic levels.

rows are numbered by a new "cubic" quantum number N which may be supposed to take on the same set of values as M_L. N has no obvious physical meaning, but served to identify the roots W_N in the cubic field according to the scheme

$$W_{-3} = W_0 = W_3 = 0, \; W_{-2} = W_{-1} = W_1 = -8Dq, \; W_2 = -18Dq.$$

The relations (2) show that the transformation which diagonalizes the terms in D will factorize the orbital problem into three quadratics and a singlet. These are

$$\begin{vmatrix} 6(\sigma-\delta) & -(15)^{1/2}(3\sigma+\delta) \\ -(15)^{1/2}(3\sigma+\delta) & -8Dq \end{vmatrix} \quad \begin{vmatrix} -8Dq & (15)^{1/2}(3\sigma-\delta) \\ (15)^{1/2}(3\sigma-\delta) & 6(\sigma+\delta) \end{vmatrix}$$

$$\begin{vmatrix} -8Dq & -2(15)^{1/2}\delta \\ -2(15)^{1/2}\delta & -12\sigma \end{vmatrix} \qquad -18Dq$$

We denote the roots of these by (r_{-3}, r_{-1}), (r_1, r_3), (r_{-2}, r_0) and r_2, where the suffix is a new "rhombic" quantum number taking on the same values as N or M_L. This set of roots is, of course, invariant if the coefficients of the rhombic field be permuted cyclically, $A \rightarrow B \rightarrow -(A+B)$ but they undergo the cyclic permutation $r_{-1} \rightarrow r_{-2} \rightarrow r_1$, $r_{-3} \rightarrow r_0 \rightarrow r_3$, while r_2 is invariant. Let the transformation matrices which diagonalize these quadratics for given values of D, A and B be

$$\begin{array}{r|rr} & -3 & -1 \\ \hline -3 & r & s \\ -1 & -s & r \end{array} \qquad \begin{array}{r|rr} & 1 & 3 \\ \hline 1 & t & u \\ 3 & -u & t \end{array} \qquad \begin{array}{r|rr} & -2 & 0 \\ \hline -2 & p & q \\ 0 & -q & p \end{array} \qquad \begin{array}{r|r} & 2 \\ \hline 2 & 1 \end{array} \tag{4}$$

The values of the elements can be calculated for any given values of D, A and B. The columns are numbered by the "cubic" quantum number N and the rows by the "rhombic" quantum number Q. We now introduce the spin and have to differentiate between Ni, Cr and Co.

NICKEL

Mathematical theory

For nickel $S=1$, so that $M_S = -1, 0, 1$. The secular determinant, of order 21, breaks up into one of the tenth and one of the eleventh order, involving, respectively, even and odd values of $M = M_L + M_S$. This follows since the complete Hamiltonian contains only terms of the type $\Delta M = 0, \pm 2, \pm 4$. We are interested primarily in the root $-18Dq$ which lies below the others. It occurs once (with $M_S = 0$) in the eleventh order determinant, and twice ($M_S = \pm 1$) in the tenth order determinant. Transforming the eleventh order determinant to the (N, M_S) representation, we require the element

$$\mathcal{H}(2, 0; N', M_S') = T(2, 0; M_L, 0)\, \mathcal{H}(M_L, 0; M_L', M_S') R^{-1}(M_L', M_S'; N', M_S'),$$

where R stands for S if $M_S' = \pm 1$, and for T if $M_S' = 0$. We have included the quantum number M_S in T and R as though they were diagonal in M_S. They are indeed independent of M_S. In the N, M_S representation the only nonvanishing elements of the orbit-spin and magnetic energies are found to be

$$\mathcal{H}(2,0;1,1) = \mathcal{H}(2,0;-1,1) = \mathcal{H}(2,0;1,-1) = -\mathcal{H}(2,0;-1,-1) = (2)^{1/2}\lambda$$
$$\mathcal{H}(2,0;-2,0) = 2\omega.$$

We know from (1) that the diagonalization of the orbit-spin terms involves the solution of cubic equations, so that it is simpler to diagonalize rhombic field terms instead. This is accomplished by the matrices (4). The relevant matrix elements in the (Q, M_S) system of representation are

$$\begin{aligned} \mathcal{H}(2, 0; -3, -1) &= \mathcal{H}(2, 0; -3, 1) = (2)^{1/2}\lambda S, \\ \mathcal{H}(2, 0; -1, -1) &= \mathcal{H}(2, 0; -1, 1) = (2)^{1/2}\lambda r, \\ \mathcal{H}(2, 0; 1, -1) &= \mathcal{H}(2, 0; 1, 1) = (2)^{1/2}\lambda t, \\ \mathcal{H}(2, 0; 3, -1) &= \mathcal{H}(2, 0; 3, 1) = -(2)^{1/2}\lambda\omega, \\ \mathcal{H}(2, 0; -2, 0) &= 2\omega p, \mathcal{H}(2, 0; 0, 0) = -2\omega q, \end{aligned}$$

from which the first approximation to the energy can be found. The tenth order determinant is not quite so simple, for the root $-18Dq$ occurs twice, with $M_S = \pm 1$, the degeneracy not being removed by the rhombic field. Suppose the Hamiltonian has been transformed to the (Q, M_S) system, i.e., to the form $\mathcal{H}_0 + \lambda_0\mathcal{H}_1 + \omega_0\mathcal{H}_2$, where $\mathcal{H}_0$ is diagonal and $\mathcal{H}_1$ has no diagonal terms. Apply the transformation

$$(1 + \lambda S)(\mathcal{H}_0 + \lambda\mathcal{H}_1 + \omega\mathcal{H}_2)(1 - \lambda S + \lambda^2 S^2 + \cdots)$$

and choose S so as to make the coefficient of λ vanish in this expression. Then the Hamiltonian becomes

$$\begin{aligned} \mathcal{H}(n, m) = {} & \mathcal{H}_0(n, m) + \lambda^2 \sum \mathcal{H}_1(n, i)\mathcal{H}_1(i, m)/h\nu(n, i) + \omega\mathcal{H}_2(n, m) \\ & + \lambda\omega \sum [\mathcal{H}_1(n, i)\mathcal{H}_2(i, m)/h\nu(n, i) - \mathcal{H}_2(n, i)\mathcal{H}_1(i, m)/h\nu(i, m)] \\ & + \cdots. \end{aligned}$$

There are now terms in λ^2 on the diagonal which remove the degeneracy[15] and the coefficient of ω is altered by a term of order $\lambda|D$. We can now set up the quadratic secular problem connected with the two coincident roots, and solve it on the assumption that the magnetic field is small. The two resulting values of W,[16] together with that obtained from the eleventh order determinant, are given below.

$$\begin{aligned} & -18Dq + 4\lambda^2(\alpha_1 + \alpha_2) + \omega^2(1 + 8\lambda\alpha_1)/\lambda^2(\alpha_2 - \alpha_3) + 4\omega^2\alpha_1, \\ & -18Dq + 4\lambda^2(\alpha_1 + \alpha_3) - \omega^2(1 + 8\lambda\alpha_1)/\lambda^2(\alpha_2 - \alpha_3) + 4\omega^2\alpha_1, \\ & -18Dq + 4\lambda^2(\alpha_2 + \alpha_3) \qquad\qquad\qquad\qquad\qquad\qquad + 4\omega^2\alpha_1. \end{aligned}$$

Here

$$\begin{aligned} \alpha_1 &= p^2/(r_2 - r_{-2}) + q^2/(r_2 - r_0), \\ \alpha_2 &= r^2/(r_2 - r_{-1}) + s^2/(r_2 - r_3), \\ \alpha_3 &= t^2/(r_2 - r_1) + u^2/(r_2 - r_3). \end{aligned}$$

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[15] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

[16] There are actually first order terms in the magnetic field of order $(\lambda^2/\text{cubic sepn.})^2$ but the contribution of these to the susceptibility is so small that they can be completely neglected.

If the axes undergo a permutation represented by $A \rightarrow B \rightarrow -(A+B)$ it is readily verified that the roots r undergo a corresponding permutation, and $\alpha_1 \rightarrow \alpha_2 \rightarrow \alpha_3$. The susceptibility along the z axis is found from the general formula

$$\chi = -(N/H) \sum (\partial W/\partial H) e^{-W/kT} / \sum e^{-W/kT}.$$

On the assumption that the exponentials can be expanded, this gives

$$\chi_1 = (8N\beta^2/3kT)[1 + 8\lambda\alpha_1 + \theta_1/kT + \cdots] - 8N\beta^2\alpha_1, \tag{5A}$$

where terms in $1/T^3$ and above have been discarded, and

$$\theta_1 = 2\lambda^2(\alpha_2 + \alpha_3 - 2\alpha_1)/3.$$

The term independent of temperature arises as usual from the term in H^2 in the energy. The other two principal susceptibilities are obtained by permuting the axes cyclically, so that the mean of the three principal susceptibilities is

$$\bar{\chi} = (8N\beta^2/3kT)[1 + (8\lambda/3 - kT)(\alpha_1 + \alpha_2 + \alpha_3)], \tag{5B}$$

in which there is rigorously no term in $1/T^2$.

If the crystal field is assumed to have cubic symmetry, the lowest level has a first order effect, and the susceptibility is

$$\chi = (8N\beta^2/3kT)(1 - 4\lambda/5D) + 4N\beta^2/5D. \tag{5C}$$

Comparison with experiment

In the Hamiltonian the constant λ of the orbit-spin coupling is known, while Aa, Ba, Dq are to be determined from the observed susceptibilities. A measurement of the mean susceptibility at one temperature will enable us to determine the one parameter D if we assume as an approximation that Aa and Ba vanish. The assumption of a purely cubic field is a convenient approximation in estimating the order of magnitude of D. We shall consider later the effect of the rhombic field.

In Ni the multiplet is inverted; its over-all width is given by $|\Delta\nu| = \lambda S(2L+1)$. By using the value 2347 cm^{-1} given by Laporte[17] for $\Delta\nu$ we obtain $\lambda = -335$ cm^{-1}. The observed value 26.56×10^{-6} of the susceptibility at 170°K,[7] giving $\chi T = 45.15 \times 10^{-4}$, then leads to a value of Dq from Eq. (5) equal to 1485 cm^{-1}, which corresponds to an over-all separation due to the cubic field of the order of 3 volts. Thus according to (5) the graph of χT against T is a straight line which we have chosen to pass through the experimental point at 170°K, and which cuts the χT axis at $\chi T = 43.64 \times 10^{-4}$. If we had calculated Dq from experimental points at different temperatures, slightly different values would have been obtained. In Fig. 2 we have plotted the experimental values of χT obtained by Gorter, de Haas, and van den Handel,[7] using T as abscissa. It is seen that the experimental points, with the

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[17] O. Laporte, Zeits. f. Physik **47**, 761 (1928).

exception of those at low temperatures, lie fairly close to the theoretical curve. The relation proposed by Gorter, de Haas, and van den Handel is $\chi(T+3)=\text{const.}$ In Fig. 2 we have also plotted the experimental values of $\Delta(T+3)$ as a function of T; the approximation of this function to a constant is seen to be very poor indeed. We conclude that the observations are represented much more closely by $\chi T=\text{const.}$ than by $\chi(T+3)=\text{const.}$ It should be remembered that this method of plotting the experimental data, which is equivalent to plotting the square of the effective magneton number as a function of T, is a much more severe test than plotting $1/\chi$ against T, as is usually done.

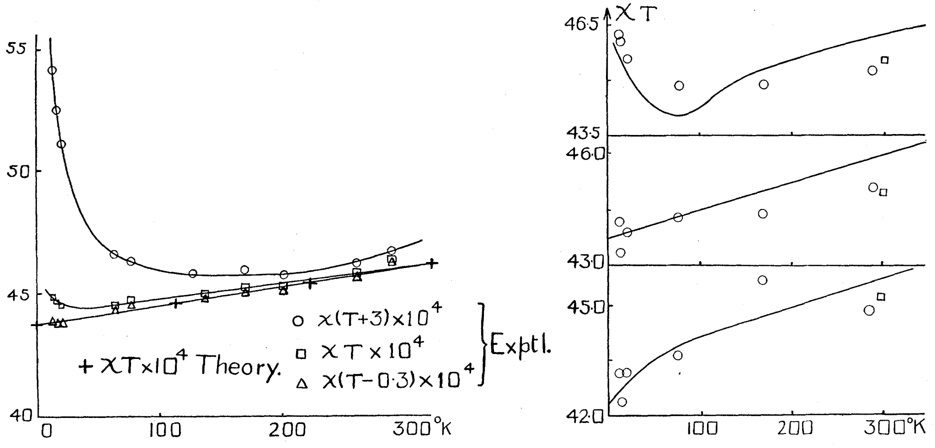

Fig. 2A. Fig. 2B.

Fig. 2. The curves in Fig. 2A serve a double purpose. In the first place they show that a formula of the type $\chi T=A+BT$ demanded by theory for Ni, represents the experimental points better than the curve $\chi(T+3\cdot 0)=\text{const.}$ given by Gorter, de Haas and v. d. Handel.[7] In the second place it is seen that the experimental values of $\chi(T-0\cdot 3)=\text{const.}$ fit the theoretical curve for χT exactly. The addition of -0.3 to T is a minor effect and perhaps represents the result of exchange forces not envisaged in the crystalline potential we have assumed. The one arbitrary parameter in the theory has been chosen to fit the observed magneton number at 170°K. The slope of the χT curve is then uniquely determined and its agreement with experiment is a good confirmation of the theory. Fig. 2B shows the theoretical principal susceptibilities χT of Ni plotted against T, and the experimental points of Jackson corrected by Gorter, de Haas and v. d. Handel,[7] which are marked in circles (see text).

There still remains the deviation of the three low temperature points from the theoretical curve. The present calculation takes no account of intermolecular actions, such as exchange effects, which are not describable by an electric field of definite symmetry. These effects are known to be capable of giving rise to a term Δ which will however be small on account of the high dilution of the salt. This correction will be important at low temperatures. If we plot $\chi(T-0.3)$ against T, the experimental points are brought to lie much more nearly on a straight line. It may be that the term $\Delta=0.3°$ is a measure of inter-molecular actions other than the crystal fields here contemplated, We must now consider the effect of the rhombic field in producing asymmetry in the principal susceptibilities. Using Rabi's[5] values for $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$ and equating them to the three expressions obtained by permuting cyclically the indices in (5A), we obtain three simultaneous equations for α_1, α_2, α_3, whose solution is

$$\alpha_1 = -7.94 \times 10^{-5}, \ \alpha_2 = -8.12 \times 10^{-5}, \ \alpha_3 = -8.29 \times 10^{-5}.$$

From these we have to determine the three parameters Dq, Aa and Ba which specify the crystal field. To set up and solve the algebraic equations connecting these parameters with the α's would be very lengthy, so we have to recourse to the method of trial and error. Thus we find that a crystal field having the Hamiltonian

$$1260(x^4 + y^4 + z^4) + 176(x^2 + 2y^2 - 3z^2)$$

gives

$$\alpha_1 = -7.96 \times 10^{-5}, \ \alpha_2 = -8.13 \times 10^{-5}, \ \alpha_3 = -8.24 \times 10^{-5}.$$

Better agreement could be obtained by using a slightly larger value of the constant of the rhombic field and by changing the ratios of the coefficients of the rhombic field, but it is not, perhaps, worth while pursuing numerical accuracy when the experimental precision is not very high. It is instructive, particularly for comparison with cobalt, to observe how little dissymmetry is produced by a comparatively large rhombic term. Thus the field given above produces an over-all separation of the cubic level Γ_4 amounting to about one-half the interval separating this cubic level from the level Γ_5. The separation produced in the level Γ_2 has an over-all width of 1.5 cm^{-1} so that the individual values of Δ for the three axes are almost negligible, and the expansions of the exponentials which we have used is legitimate even at liquid hydrogen temperatures. At extremely low temperatures Δ is relatively important and it is this fact that accounts for the different behavior of the principal χT for small values of T, shown in Fig. 2B.

Gorter, de Haas and v. d. Handel[7] have given values of the principal susceptibilities of $Ni(SO_4) \cdot 7H_2O$ using their own values of the mean susceptibility together with the differences in the principal susceptibilities found by Jackson.[6] The exactitude of these values is open to question, but to illustrate how they check with the theory we have plotted the experimental values (shown by circles) and the theoretical curves *using for the constants of the crystal field those values found for* $Ni(SO_4)_2(NH_4)_2 \cdot 6H_2O$. The agreement is very good, considering the sensitivity of the method of plotting the results, and the experimental results confirm the existence of a $1/T^2$ term for the individual axes although there is none in the mean. The values found by Rabi[5] on the ammonium salt are marked by squares. Since, as far as we can tell, the constants of the crystal field acting on the Ni ion are exactly equal in the two salts, it seems likely that the ions surrounding the Ni ions are the same and in the same relative positions in the two salts.

CHROMIUM

Chrome alum, whose susceptibility at temperatures down to that of liquid helium has been measured by de Haas and Gorter,[9] forms cubic crystals, so that no differences in the principal susceptibilities are to be expected.[18] It will be sufficient to suppose the crystal field to have cubic symmetry. Van Vleck[14] has shown that for Cr, whose ground state is ^4F, the matrix elements of $\sum_i (x_i^4+y_i^4+z_i^4)$ have the same sign as those of $(x^4+y^4+z^4)$ calculated for a single electron system; that is the coefficient q is positive. The root $-18Dq$ (Γ_2) is accordingly lowest. The secular problem inclusive of spin is of order 28; but on account of the selection rule $\Delta M=0$, ± 2, ± 4, obeyed by the Hamiltonian ($\Delta M=0$, ± 4 if the rhombic field is absent) the secular determinant breaks up into the product of two, which are identical except as regards the sign of the terms in H. This is, of course, an example of the Kramers degeneracy.[19] Reference to the diagram in Bethe[11] shows that the orbit-spin interaction is incapable of removing the degeneracy of Γ_2 in any approximation, so that we need consider only the terms in H, which give rise to first and second order Zeeman effects. Fixing our attention on one of the two secular determinants of order 14, we observe first of all that the root Γ_2 occurs twice ($N=2$, with $M_S=-\frac{1}{2}$, $\frac{3}{2}$, say). In passing from the original M_L, M_S representation to that in which the cubic field is diagonal, the spin terms $2M_S$ will of course remain on the diagonal, so that the two occurrences of the root Γ_2 have first order moments 3ω and $-\omega$ from this determinant and -3ω and ω from the other. If this were all, the magneton number would have the "spin only" value $(15)^{1/2}$, verifying that the spin is free. But we have still to consider the off-diagonal terms involving ω, which represent the contribution of the orbit, and which are diagonal in M_S. We readily find for the elements satisfying this condition

$$\mathfrak{H}(2,\, -\tfrac{1}{2};\, -2,\, -\tfrac{1}{2}) = -\lambda + 2\omega$$

$$\mathfrak{H}(2,\, 3/2;\, -2,\, 3/2) = 3\lambda + 2\omega$$

which gives for the levels in the presence of the field

$$= \omega(1 - 2\lambda/5Dq) - 2\omega^2/5Dq,$$

$$\pm 3\omega(1 - 2\lambda/5Dq) - 2\omega^2/5Dq.$$

Disregarding the high-frequency term for the moment, we obtain for the susceptibility

$$\chi = (15N\beta^2/3kT)(1 - 2\lambda/5Dq)^2.$$

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[18] The chrome alum $KCr(SeO_4)_2 \cdot 12H_2O$, which forms cubic crystals has in its absorption spectrum a narrow doublet whose separation is roughly 4 cm^{-1} (cf. K. Schnetzler, Ann. d. Physik **10,** 373 (1931)). If this doublet is due to the doubling of the basic level Γ_2, the Hamiltonian must contain non-cubic terms, besides the predominant cubic terms. This follows since the orbit-spin coupling does not decompose Γ_2. If this is so, this alum should exhibit slight asymmetry in its principal susceptibilities.

[19] H. A. Kramers, Proc. Amst. Acad. **33,** 959 (1930).

Here λ is positive, so that the magneton number should be less than the "spin-only" value, which is actually found to be the case. From the value 912 cm^{-1} given by Laporte[17] for the over-all separation of the ^4F multiplet in chromium, we deduce $\lambda = 87$ cm^{-1} and taking de Haas and Gorter's[9] value 19.02 for the Weiss magneton number of Cr, we obtain $Dq = 3730$ cm^{-1}. This justifies our neglect of the high-frequency term, which is proportional to λ/D. The experimental results do not show any trace of high-frequency effects. It is not possible to place much reliance on the above estimate of the magnitude of the separation due to the cubic field, since a small change in the experimental magneton number would produce a very considerable change in the calculated value of Dq. It need scarcely be pointed out that for Cr, as for Ni, the introduction of even a large rhombic field will not appreciably affect the isotropy of the susceptibility. As yet, however, no measurements have been made on the principal susceptibilities of Cr salts.

COBALT

Mathematical theory

It may be stated here that our calculations on Co are not as complete as those on Ni and Cr, but the difficulties are only in the numerical computation. There seems to be no doubt, however, that good agreement with experiment could be obtained by a more exhaustive trial-and-error procedure. The ground state of cobalt is ^4F, and the secular determinant is of order 28. On account of the Kramer's degeneracy, it breaks up into two determinants of order 14, identical except for the sign of the terms in the magnetic field. The orbital part of the problem is the same as for nickel, where the ground state was also an F state, so that in a cubic field the roots are 0, $-8Dq$, $-18Dq$. On account of the inversion discussed above, the level 0 (denoted Γ_4 above) is now lowest, and occurs six times in each secular determinant of order 14, namely, with $N = -3, 0, 3$ and $M_S = \frac{3}{2}, \frac{1}{2}$ or $-\frac{3}{2}, -\frac{1}{2}$. The portion of the determinant involving these roots, which coincide in the absence of a rhombic field and orbit-spin coupling, is

$$\begin{matrix} 6B - 3l\omega & -3m + 3\omega/2 & 0 & 0 & n & 0 \\ -3m + 3\omega/2 & 6A - 3l\omega & 0 & 0 & -n & 0 \\ 0 & 0 & 6B + l\omega & m + 3\omega/2 & 2m & n \\ 0 & 0 & m + 3\omega/2 & 6A + l\omega & 2m & -n \\ n & -n & 2m & 2m & 6C - \omega & 0 \\ 0 & 0 & n & -n & 0 & 6C + 3\omega \end{matrix} \tag{6}$$

Here $l = 1 + 15\lambda/32D$, $m = 3\lambda/4$, $n = 3(3)^{1/2}\lambda/4$. Interaction between the levels $0, -8Dq$, $-18Dq$ has been taken account of with sufficient accuracy by the diagonal terms in $\omega\lambda/D$. This amounts to discarding the high-frequency part of the susceptibility; if we do this we may restrict ourselves to this sixth order determinant in calculating the levels. As the sextic secular equation is not soluble when the rhombic field is comparable with the orbit-spin coupling, we must assume that the former is much smaller than the latter or *vice-versa*. Our calculations indicate that the two influences are in fact of comparable magnitude, which makes close numerical agreement difficult to obtain without more elaborate computations. Here we deal with the two extreme cases only.

Orbit-spin greater than rhombic field

Consider first the case where the orbit-spin coupling is greater than the rhombic field. The orbit-spin interaction alone is capable of partially removing the degeneracy in (6). When we do not restrict ourselves to interactions within the sextet the degeneracy which survives the cubic field and the orbit-spin interaction is given by the resolution $\Gamma_4 D_{3/2} = \Gamma_6 + \Gamma_7 + 2\Gamma_8$, i.e., two singlets and a quadratic occurring twice. When we restrict ourselves to interactions within the sextet the degeneracy must at least be as great as this, which ensures that the sextet will have simple roots when σ, δ, ω all vanish. These are readily found to be $15\lambda/4$, $3\lambda/2$ (twice), $-9\lambda/4$ (three times), and the corresponding form of the sextet, with these roots on the diagonal, can easily be written down. The energy levels in the presence of the magnetic field have now to be found on the assumption that the rhombic field is small compared with the orbit-spin interaction. In cobalt $\lambda = -180$ cm^{-1} so that the triply degenerate level $-9\lambda/4$ will have such a small Boltzmann factor that its contribution to the susceptibility may be neglected even at room temperatures; this level does not affect the moment of the level $15\lambda/4$, and in calculating its influence on the moment of the levels $3\lambda/2$, which is relatively less important in any case, we may suppose it to remain undecomposed by the rhombic field. But in obtaining the moments of the two levels $3\lambda/2$, it is necessary to allow the rhombic field to remove this degeneracy. We have calculated the level $15\lambda/4$ correct to a third order approximation and the two levels $3\lambda/2$ to a second order approximation.[20] The calculation is straightforward but too elaborate to be given here. To illustrate the type of result obtained, we give the energy levels in the presence of the magnetic field only for the lowest level, correct to a second order perturbation calculation. For brevity the third order terms have been omitted. We find

$$W = 15\lambda/4 - \omega(13/6 + 5\lambda/8D) + [(36\sigma - 35\omega - 165\lambda\omega/16D)^2 + 432\delta^2]/405\lambda + \cdots.$$

The expressions for the other levels are of the same type.

At sufficiently low temperatures the square of the effective Bohr magneton number $n_B^2 = 3\chi kT/N\beta^2$ is given by three times the square of the coefficient of the term in H. Hence, if we extrapolate the experimental values of χT to $T=0$, we obtain three equations which theoretically enable us to determine σ, δ and D. The values obtained in this way are however so sensitive to variations in χT at $T=0$ within the range of possible error that it is

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[20] The details of the inclusion of the third order terms in the perturbation problem will be considered by Mr. Jordahl in his paper on Cu.

preferable to proceed differently. The argument of Van Vleck[4] shows that if the cubic field acting on the metallic ion be the same in nickel ammonium sulphate as in cobalt ammonium sulphate the constant Dq has the same value numerically. We accordingly assume $Dq = -1200$ cm^{-1}, thereby giving up the possibility of obtaining values of σ and δ for arbitrarily given values of $(\chi T)_0$; instead we assume values for σ and δ and calculate the susceptibilities at various temperatures. The values which have been chosen for illustration are $\sigma = \delta = 20$, corresponding to a term $40(x^2 - z^2)$ in the Hamiltonian, which gives roughly the right degree of asymmetry. It is of course possible to choose different values for the individual coefficients of x^2, y^2, z^2, but the computations are laborious and do not give any new information. Two points deserve mention. In the first place, a much smaller rhombic field is required in cobalt salts to produce the observed asymmetry than is needed for nickel salts despite the much greater isotropy of the latter. In the second place the calculated mean susceptibility for the three orientations is consistently greater than that observed. Fig. 3A shows the calculated values of $n_B{}^2 = 3kT\chi/N\beta^2$ plotted against T for the three magnetic axes of $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The trend of these curves may readily be understood in a qualitative way. At low temperatures the only level contributing to the susceptibility is the lowest. Since this has both a first and a second order Zeeman effect $\chi T = a + bT$, a and b being constants. At higher temperatures the two states $3\lambda/2$ begin to contribute to the susceptibility, but this is counteracted by the depopulation of the lowest level; these higher levels have smaller Zeeman effects than the levels $15\lambda/4$ so that the curve of χT against T rises less steeply and tends to an almost constant value. At still higher temperatures the three levels $-9\lambda/4$ would also contribute to the susceptibility but these temperatures are not reached experimentally.

The value of $n_B{}^2$ is plotted also for the case where there is no rhombic field and this curve is shown dotted in Fig. 3A. It should be noticed that the effect of the rhombic field is to produce asymmetry and also to lower the mean value of the three principal susceptibilities.[21] Unfortunately, it is not within the limits of the present approximation to make the rhombic field sufficiently large to give agreement with experiment, as then the convergence would be poor. It is very reasonable, however, to suppose that a larger

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[21] Let us imagine the magnitude of the rhombic field is varied from a very large value down to zero. The behavior of the three principal susceptibilities is as follows. Orientation (3) starts at the "spin only" value, decreases and then starts to increase again, finally ending on the curve for zero rhombic field shown in Fig. 3A. Orientation (2) starts slightly above the "spin only" value due to the introduction by the orbit spin coupling of small diagonal elements in the orbital angular momentum, representing the contribution of the higher cubic levels, and then decreases at low temperatures but increases at higher temperatures, ending finally with (3). Orientation (1) is rather complicated. It starts with (2) but the susceptibility increases rapidly with decreasing rhombic field, and develops a hump at low temperatures. This is because for this orientation the lowest level has a large first order Zeeman effect. The susceptibility then begins to fall again, passing through a representative curve shown in Fig. 3B. The hump fades out, the susceptibility decreasing at low and increasing at high temperatures, finally ending with (2) and (3).

rhombic field would give good agreement with experiment, except possibly at low temperatures. Since the only measurements at low temperatures are those of Jackson,[6] made as long ago as 1922, and which at other temperatures are known to be greatly in error, this discrepancy is not worth considering. When better experimental data are available another effort will be made to obtain a better solution of this troublesome sextet.

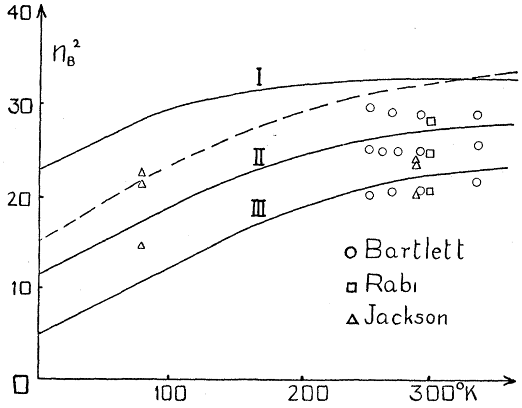

Fig. 3A.

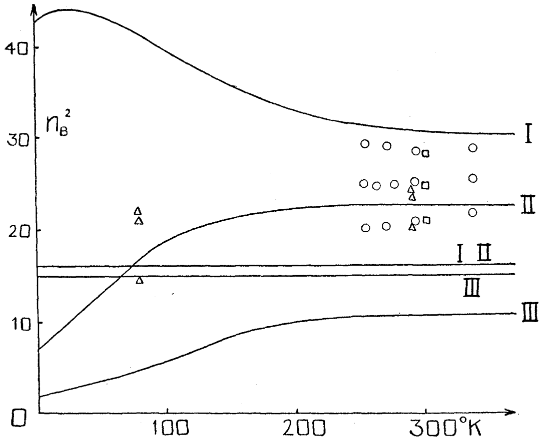

Fig. 3B.

Fig. 3. The heavy lines in Figs. 3 show the calculated values of n_B^2 for Co $(NH_4)_2(SO_4)_2 \cdot 6H_2O$ for the two rhombic fields (3A) $40(x^2-z^2)$ (3B) $200(x^2-z^2)$, while for comparison, the experimental points obtained by different observers are given. The numbers on the curves denote the axes to which the curves refer. The dotted lines in Fig. 3A is for zero rhombic field; the horizontal straight lines in Fig. 3B are for extremely large rhombic fields. It is reasonable to suppose that a rhombic field intermediate to the values we have taken would give agreement with experiment. It is significant that the results of Bartlett[8] along axis (1) do actually seem to be falling with increasing T, as would be the case for an intermediate field. The agreement at low temperatures is not good but the experimental values are those of Jackson[6] and may easily be in error.

Rhombic field greater than orbit-spin

In the hope that a perturbation calculation from the other limiting case would be more effective, calculations were also made from this end. Here the orbit spin is subsidiary to the rhombic field. The rhombic field can be seen to decompose the sextuply degenerate level into three doubly degenerate ones, with separations proportional to the coefficients of the rhombic field. The orbit-spin interaction does not remove the remaining degeneracy in the first approximation, but only in the second. Expressions for the energy levels and their first and second order Zeeman effects can be written down, and the susceptibility calculated for given values of the constants D, A, B, C of the crystal field, such that the rhombic field alone produces a separation which is small compared with that due to the orbit-spin alone. In the absence of the spin the energy levels are $6Aa$, $6Ba$, $-6a(A+B)$. We suppose that $-6a(A+B)$ lies below $6Aa$ and $6Ba$ and calculate the Zeeman effects of the two lowest roots correct to a third approximation, retaining terms in the magnetic field up to H^2, in the usual way. The Zeeman effects are different according as the magnetic field acts along the x, y, or z axes. The exact expressions are long, but for illustration we give the two lowest roots, when the magnetic field acts along the x, y and z axes, correct only up to a second order perturbation calculation. For brevity the third order terms have been omitted.

$$\left.\begin{aligned} W_\pm(x) &= W_\pm - \omega_+[1 \pm (\alpha + 2\beta)\theta] \pm 2\omega_+{}^2\alpha^2\theta^3/3\lambda^2, \\ W_\pm(y) &= W_\pm - \omega_-[1 \mp (2\alpha + \beta)\theta] \pm 2\omega_-{}^2\beta^2\theta^3/3\lambda^2, \\ W_\pm(z) &= W_\pm + \omega[1 \pm (\alpha - \beta)\theta] \pm 2\omega^2\theta^3(\alpha + \beta)^2/3\lambda^2 \end{aligned}\right\}$$

where

$$\begin{aligned} W_\pm &= -6a(A + B) + 45\lambda^2(\beta - \alpha)/16 \pm 9\lambda^2\theta/4, \\ \theta &= (\alpha^2 + \beta^2 + \alpha\beta),\ \omega_+ = \omega(1 + 9\lambda/128D + 9\lambda\beta/4), \\ \omega_- &= \omega(1 + 9\lambda/128D - 9\lambda\alpha/4). \end{aligned}$$

We have written $\alpha = 1/6a(B-C)$ and β, γ for the cyclic permutations. From these expressions the principal susceptibilities may be calculated. For illustration, a rhombic field represented by $200(x^2-z^2)$ in the Hamiltonian has been taken. The result is shown by the curves in Fig. 3B. It is readily verified that the curves correspond with those in Fig. 3A as shown by the numbering. The values of $n_B{}^2$ for a very large rhombic field are also shown by the horizontal straight lines. These are only limiting curves, however, since we have assumed the cubic field to predominate and therefore we cannot make the rhombic field as large as we please.

We have now calculated the susceptibilities (*i*) for a rhombic field $40(x^2-z^2)$ (*ii*) for a rhombic field $200(x^2-z^2)$, inclusive of orbit-spin coupling in both cases. The latter alone produces an over-all splitting of the level Γ_4 of the cubic field amounting to roughly 1000 cm^{-1}, while the separations produced by fields (*i*) and (*ii*) are respectively 480 cm^{-1} and 2400 cm^{-1}. The principal susceptibilities calculated on the basis of field (*i*) show roughly the right degree of asymmetry, but are too high. Interpolating between (*i*) and (*ii*), it seems that a rhombic field of magnitude intermediate between (*i*) and (*ii*), but much nearer (*i*), will give good agreement with experimental values, except possibly at low temperatures, where however, the experimental values are in considerable doubt. Neither of the two methods of approximation used above are applicable in this intermediate region and the calculation would consist in the numerical solution of the original sextic secular equation.

It is interesting to notice that there would have been no gain in generality if we had added to the Hamiltonian terms representing a field of tetragonal symmetry or terms of rhombic symmetry of higher degree, provided the field of cubic symmetry always predominates. In order to see this we need only observe that in the orbital problem the lowest level Γ_4 of the cubic field is split by the rhombic field into the three levels G_2, G_3, G_4, no two of which belong to the same representation of the rhombic group. Consequently it is not possibly to change the moments of these levels by changing the type of rhombic field nor can this be accomplished even by the superposition of a tetragonal field, since this is only a particular form of rhombic field. Because the moments are fixed, the susceptibility can be changed only through the relative position of the energy levels and as there are three levels, it needs only two parameters to specify them. The two parameters A and B are capable of doing this.

CONCLUSION

In the present paper no account has been taken of the variation with temperature of the constants of the crystal field. The very small changes in interatomic distances caused by thermal expansion may possibly affect these constants quite appreciably because the force between ions in a crystal is known to vary very rapidly with the distance. We have moreover assumed that the principal axes of the various types of crystalline fields all coincide. Perhaps a better approximation to the actual state of affairs would be to assume fields of different symmetry, whose principal axes were inclined to each other, the relative orientations depending on temperature in some complicated way. There would then arise the possibility of an explanation of the results of Bartlett,[8] who finds that the orientation of the principal susceptibilities relative to the crystallographic axes depend on temperature, the total variation being of the order of 5 degrees in a range of temperature 100°C.

From the considerations developed in this and the preceding paper, it should be evident that it is only rarely that the constant Δ of the experimenters has any theoretical interpretation. In order that it may have, it is necessary that the expansion $\chi = C/T - C\Delta/T^2 + \cdots$, should converge very rapidly. This condition may be expressed in another form, that the Stark separations of the levels contributing to the susceptibility should be small compared with kT. This is not satisfied in the rare earths nor with Co but our calculations have shown that it is satisfied with Ni and Cr. That the susceptibility of the rare earths can be represented by the Curie-Weiss law is merely fortuitous. Even here the value of Δ obtained depends on the temperature at which the measurements are made and in this sense Δ has no theoretical significance.

One of the most surprising facts revealed by our calculations of the susceptibilities in crystals is that a field of cubic symmetry should be capable of allowing such excellent agreement to be obtained with experiment. At first sight there seems to be no reason whatever for the field to possess cubic, or even nearly cubic, symmetry. In the case of Ni it was definitely established that a field predominantly rhombic and of the form $Ax^2+By^2-(A+B)z^2$, was incapable of giving the observed principal susceptibilities. The next assumption is naturally a field of cubic symmetry together with a much smaller rhombic term, an assumption which has proved completely successful with Ni, Cr and Co. For the rare earths, where measurements of the principal susceptibilities are lacking, and only the variation with temperature of the mean susceptibility has been observed, good agreement with experiment is obtained on the assumption of a cubic field alone. Without understanding why complicated crystals should have such simple crystalline fields, it must at least be conceded that the evidence in favor of a predominant field of cubic symmetry is strong. Whether or not there are other types of field which will give equally as good agreement with experiment remains to be seen.

In our calculations of paramagnetic susceptibilities, both of the rare earths and of the elements of the iron group, the sign of D in Eq. (3) has been consistently positive. In a Letter to the Editor[22] Gorter finds that this choice of the sign of D agrees with there being water molecules (or else oxygen ions) arranged at the corners of an octahedron around the paramagnetic ion.

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[22] C J. Gorter, Phys. Rev. **42**, 437 (1932).