PHYSICAL REVIEW VOLUME 140, NUMBER 5A 29 NOVEMBER 1965

Magnetic and Thermal Properties of $[Cr_3(CH_3COO)_6(OH)_2]Cl \cdot 8H_2O$, a System of Clusters of Three Cr^{3+} Ions*

Norikiyo Uryû† and S. A. Friedberg
Carnegie Institute of Technology, Pittsburgh, Pennsylvania

(Received 2 July 1965)

The paramagnetic susceptibility and magnetic specific heat of the complex salt $[Cr_3(CH_3COO)_6(OH)_2]$-$Cl \cdot 8H_2O$ are examined theoretically in the light of recently obtained knowledge of its crystal structure. Each unit cell contains four isolated triangular clusters of three Cr^{3+} ions. The crystal properties may be calculated from the Hamiltonian of a single cluster. The structural evidence neither confirms nor excludes clearly the long-conjectured possibility that a cluster has less than trigonal symmetry. In an attempt to construct possible alternatives to Kambe's theory which requires cluster distortion, the energy levels of a cluster have been calculated assuming equal isotropic exchange interaction, $J_0[(\mathbf{S}_1 \cdot \mathbf{S}_2)+(\mathbf{S}_2 \cdot \mathbf{S}_3)+(\mathbf{S}_3 \cdot \mathbf{S}_1)]$, among the Cr^{3+} ions ($S=\frac{3}{2}$), each of which experiences an axial crystalline field. In order to split the two Kramers doublets comprising the ground state as required by experiment and retain the cluster symmetry, a higher order spin interaction is required of the form $J'[(\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_2 \cdot \mathbf{S}_3)+(\mathbf{S}_2 \cdot \mathbf{S}_3)(\mathbf{S}_3 \cdot \mathbf{S}_1)+(\mathbf{S}_3 \cdot \mathbf{S}_1)(\mathbf{S}_1 \cdot \mathbf{S}_2)]$. Fitting the low-temperature specific heat and susceptibility one finds $J_0=30k$ and $J'=0.9k$, with a slightly smaller value of J' required to fit the susceptibility at higher temperatures. The plausibility of such a novel interaction is considered, as is the ordered spin arrangement within a cluster at low temperatures.

1. INTRODUCTION

The magnetism of various kinds of hydrated salts of iron group ions has been extensively studied. In spite of the fact that compounds of this kind usually have complicated crystal structures, the macroscopic magnetic properties of some of them can be described quite adequately by one-ion Hamiltonians in which the influence of the crystalline field due to surrounding anions is taken into account. The exchange or dipolar interactions among magnetic ions in such materials play important roles only at very low temperatures. Typical examples are the alums and the Tutton salts. However, there are other kinds of hydrated salts of iron group ions in which two or three magnetic ions form isolated clusters and the macroscopic properties must be described by means of a pair or cluster Hamiltonian. The classic example of a salt containing isolated pairs of magnetic ions is copper acetate monohydrate, $Cu(CH_3COO)_2 \cdot H_2O$. Bleaney and Bowers[1] gave an explanation of its anomalous paramagnetism by considering an isolated pair model which was later confirmed as a realistic one from the crystallographic point of view.[2]

We shall be concerned in this paper with the properties of a system composed of clusters of three paramagnetic ions. Numerous examples of such systems are thought to exist[3] but only a few have been studied in any detail. Kambe[4] first proposed a model of exchange-coupled clusters of three ions to explain the unusually large Weiss constants in complex acetates of trivalent iron and chromium which had been measured by Welo[5] in the temperature range 200∼300°K. Similar theoretical work was later done by Abragam *et al.*[6] and Yvon *et al.*[7] after Foëx, Tsai, and Wucher[8,9] extended the magnetic measurements to the helium-temperature region. Wucher and co-workers[10,11] have investigated extensively the thermal and magnetic properties of $[Cr_3(CH_3COO)_6(OH)_2]Cl \cdot 8H_2O$ and have reasonably explained their observations by using the intracluster exchange integrals as adjustable parameters. Recently, magnetic measurements on this material have been extended down to 0.5°K.

The success of Kambe's cluster model in describing the properties of $[Cr_3(CH_3COO)_6(OH)_2]Cl \cdot 8H_2O$ is particularly striking in view of the fact that the structures of this compound and of all other related salts were then unknown. Several assumptions were found necessary in the theory: (1) The orbital angular momentum of the Cr^{3+} ion is quenched by a crystalline field of sufficiently low symmetry, i.e., instead of the free-ion ground state, ${}^4F_{3/2}$, one has effectively a ${}^4S_{3/2}$ ground state for Cr^{3+}. (2) Intercluster interaction may be ignored. (3) Of the three isotropic intracluster exchange integrals, J_{12}, J_{23}, J_{31}, one is different from the other two, i.e., $J_{12}=J_{23}\neq J_{31}$ but all are antiferromagnetic.

---

* Work supported by the National Science Foundation and the U. S. Office of Naval Research.

† On leave from Department of Applied Science, Faculty of Engineering, Kyushu University, Fukuoka, Japan.

[1] B. Bleaney and K. D. Bowers, Phil. Mag. 43, 372 (1954).

[2] J. N. Van Niekerk and F. R. L. Schoening, Nature 171, 36 (1953); Acta Cryst. 6, 227 (1953).

[3] J. S. Smart in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. III, p. 63.

[4] K. Kambe, J. Phys. Soc. Japan 5, 48 (1950).

[5] L. A. Welo, Phys. Rev. 32, 320 (1928); Phil. Mag. 6, 481 (1928).

[6] A. Abragam, J. Horowitz, and J. Yvon, J. Phys. Radium 13, 489 (1952).

[7] J. Yvon, J. Horowitz, and A. Abragam, Rev. Mod. Phys. 25, 165 (1953).

[8] G. Foëx, B. Tsai, and J. Wucher, Compt. Rend. 233, 1432 (1951).

[9] B. Tsai and J. Wucher, J. Phys. Radium 13, 485 (1952).

[10] J. Wucher and J. D. Wasscher, Physica 20, 721 (1954).

[11] J. Wucher and H. M. Gijsman, Physica 20, 361 (1954).

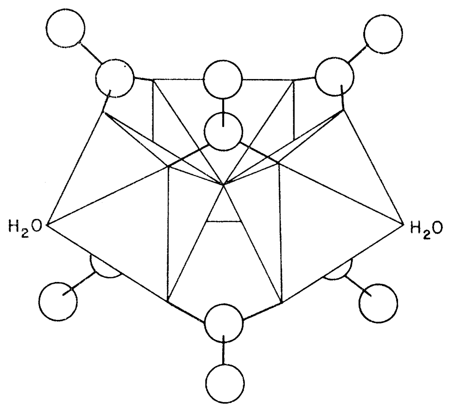

FIG. 1. Structure of $[Cr_3(CH_3COO)_6(OH)_2]Cl\cdot 8H_2O$. A chromium ion is located at the center of each one of the three octahedra. An octahedron consists of four oxygen atoms (of acetate groups), a water molecule, and an oxygen ion situated at the center of the molecule. Circles denote carbon atoms.

Very recently, Chang and Jeffrey[12] have determined by x-ray methods the structure of $[Cr_3(CH_3COO)_6(OH)_2]Cl\cdot 8H_2O$. Macroscopically, the crystal is orthorhombic. Its unit cell contains four formula units, i.e., four three-ion clusters, and has the dimensions $a=13.7$ Å, $b=24.2$ Å, and $c=9.2$ Å. The space group is found to be $P2_12_12$. As is shown in Fig. 1, the three Cr^{3+} ions comprising a cluster lie, to a first approximation, at the vertices of an equilateral triangle. Each Cr^{3+} ion is at the center of an octahedron formed by four oxygen atoms belonging to acetate groups and lying in the same plane, an H_2O molecule, and an $O^{=}$ ion. The $O^{=}$ ion is common to the octahedra surrounding each of the three Cr^{3+} ions in a cluster. The metallic ions of each cluster are well-separated from those of neighboring clusters.

In view of this structural evidence, assumptions (1) and (2) of the original theory appear quite reasonable. Assumption (3), namely the inequality of the intracluster exchange integrals, would seem, however, to be by no means an obvious consequence of the structure. In order to appreciate the implications of this assumption it is helpful to summarize the results of the earlier calculations.

Kambe took the Hamiltonian of a cluster of three ions of spin $\mathbf{S}_1$, $\mathbf{S}_2$, and $\mathbf{S}_3$ coupled by isotropic exchange to be

$$\mathcal{H}=J_0(\mathbf{S}_1\cdot\mathbf{S}_2+\mathbf{S}_3\cdot\mathbf{S}_1)+(J_0+J_1)\mathbf{S}_2\cdot\mathbf{S}_3, \qquad (1)$$

where for Cr^{3+} ions, $S_1=S_2=S_3=\frac{3}{2}$. The energy eigenvalues for this Hamiltonian can be obtained by means of arguments based on a vector model and are found to be

$$E=\tfrac{1}{2}J_0S(S+1)+\tfrac{1}{2}J_1S'(S'+1)+\text{const}, \qquad (2)$$

where $\mathbf{S}$ is the total spin and $\mathbf{S}'$ is the resultant of $\mathbf{S}_2$ and $\mathbf{S}_3$. The complete energy level diagram is shown in Fig. 2(a) for $J_0>0$, i.e., antiferromagnetic, and for $J_1=0$ and $J_1\neq 0$. The effect of making $J_1\neq 0$ is to remove some of the degeneracies appearing in this problem when all interactions are assumed equal. In particular, the lowest state of total spin $S=\frac{1}{2}$ consists of two Kramers doublets which are degenerate unless $J_1\neq 0$.

Using the cluster eigenvalues, Eq. (2), one can compute the magnetic susceptibility and the magnetic contribution to the specific heat as functions of the temperature. It is found that the best fit of the powder susceptibility data below 300°K is obtained for $J_0=30k$ and $J_1=7.5k$, although the experimental uncertainty appears rather large at high temperatures. It should be noted that the theoretical powder susceptibility is insensitive to the choice of J_0 or J_1 below ~5°K. On the other hand, the theoretical specific heat curve is quite sensitive to these parameters in this region, the closest fit being obtained for $J_0=30k$ and $J_1=4k$. Agreement between theory and experiment in this case is destroyed if J_1 is allowed to be as large as $7.5k$. This suggests perhaps that J_1 is a function of temperature. From attempts to fit the helium-temperature heat-capacity data by adjusting J_0 and J_1, it is clear that J_1

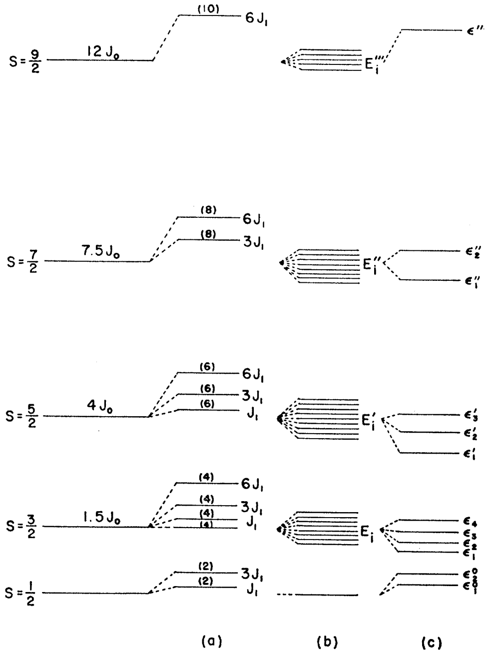

FIG. 2. Energy-level splittings for three spins of $S=\frac{3}{2}$ with: (a) one of the interactions among three spins different from the other two (Wucher and Gijsman), (b) crystalline field, (c) higher order exchange interaction.

---

[12] S. C. Chang and G. A. Jeffrey (private communication). Professor Jeffrey has proposed that a more suitable formula for this molecule should be $[O\cdot Cr_3(CH_3COO)_6\cdot 3H_2O]^+Cl^-\cdot 6H_2O$. An oxygen having trigonal planar $[sp^2]$ bonds and an occupied nonbonding $2p$ orbital is located at the center of the molecule. During the preparation of this report we learned that similar conclusions about the structure of this compound had been reached independently by B. N. Figgis and G. B. Robertson, Nature **205**, 694 (1965). The observed structure is essentially as predicted by L. E. Orgel, *ibid.* **187**, 504 (1960).

must be different from zero, i.e., that the two Kramers doublets comprising the cluster ground state must be split. This splitting amounts evidently to about $8k$ at low temperatures.

If the structure of $[Cr_3(CH_3COO)_6(OH)_2]Cl\cdot 8H_2O$ at low temperatures approximates that determined at room temperature, it becomes rather difficult to imagine that one of the intracluster exchange integrals should differ by as much as 25% from the other two. Departures of a cluster from trigonal symmetry are certainly suggested by the x-ray work, but these are quite small. If further distortion were to occur with falling temperature it is quite possible that distortions of the required size might appear and with them degeneracy removal such as has been noted above for the lowest pair of Kramers doublets. Distortion accompanied by removal of all but Kramers degeneracy is, of course, expected on the basis of the Jahn-Teller theorem. Typically, however, this mechanism is expected to separate spin components of an orbitally nondegenerate state[13] by amounts of the order of $0.1k$.

We have felt it to be of some interest, in view of the approximate nature of the Kambe model, to consider alternative possibilities. With the structural evidence at hand, it becomes reasonable now to include explicitly the effect of the crystalline field at the site of each Cr^{3+} in a cluster. Furthermore, it becomes desirable to consider, at least as a first approximation, the possibility that the usual isotropic exchange integrals within one cluster are all equal. As we shall see, this program will lead us inevitably to consider the addition to the cluster Hamiltonian of terms capable of removing the degeneracy of the two Kramers doublets constituting the ground state, just as in Kambe's problem. We shall, however, pursue in some detail the possibility of removing this degeneracy while retaining the equivalence of the three Cr^{3+} ions in a cluster.

In the following sections we develop, first of all, the quantum mechanical theory of a symmetrical cluster of three Cr^{3+} ions each of which is located at the center of an octahedron of ligands, as described above, and experiences, in addition to a cubic crystal field, a field of axial symmetry. We shall assume the Hamiltonian for a cluster to have the following form:

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}', \tag{3}$$

where

$$\mathcal{H}_0=J_0(\mathbf{S}_1\cdot\mathbf{S}_2+\mathbf{S}_2\cdot\mathbf{S}_3+\mathbf{S}_3\cdot\mathbf{S}_1) \tag{4a}$$

and

$$\mathcal{H}'=\sum_{i=1}^{3} D_i[(S_i^{\zeta_i})^2-\tfrac{1}{3}S_i(S_i+1)]. \tag{4b}$$

The axial field is assumed to act along the tetragonal axis of each octahedron as indicated in Fig. 3. The crystalline field coefficient D_i, taken to be the same for each Cr^{3+} ion, is defined in the orbital singlet ground state assuming that the separation between the ground and first excited orbital states is much larger than kT as well as any spin splitting of the orbital ground state.

We shall obtain first the eigenfunctions of the unperturbed Hamiltonian $\mathcal{H}_0$. For purposes of comparison with Kambe's results for the vector model, the energy eigenvalues are calculated for both the unperturbed problem and the case in which one of the exchange integrals differs from the other two. This is done treating the term $J_1\mathbf{S}_2\cdot\mathbf{S}_3$ as a perturbation and yields results identical with those already cited. Then we shall calculate the energy eigenvalues and eigenfunctions for a cluster treating the axial field, i.e., $\mathcal{H}'$, as a perturbation. These results will be used to calculate the susceptibility and specific heat of a salt composed of clusters and an attempt made to fit the data for $[Cr_3(CH_3COO)_6(OH)_2]Cl\cdot 8H_2O$. It will be shown that this is not possible for reasonable values of the crystalline field parameter. As with the Kambe model, the difficulty here is again the absence of splitting of the two Kramers doublets comprising the ground state. We then proceed to consider a higher order spin coupling which removes this degeneracy while preserving the symmetry of the cluster. Treating the additional terms introduced into the cluster Hamiltonian as essentially phenomenological, it will be shown that quite good agreement with the experimental data may be achieved. Finally, we shall discuss briefly the problem of the ordered spin arrangement within a cluster at very low temperatures.

2. EIGENFUNCTIONS OF THE UNPERTURBED SYSTEM

We shall denote as $\Psi_{S_iM_i}$ the eigenfunction of the spin angular momentum $\mathbf{S}_i(S_i=\frac{3}{2})$ and its z component M_i. The eigenfunction has been chosen so as to satisfy the following relations:

$$\mathbf{S}_i^2\Psi_{S_iM_i}=S_i(S_i+1)\Psi_{S_iM_i}, \tag{5a}$$

$$S_i^z\Psi_{S_iM_i}=M_i\Psi_{S_iM_i}, \tag{5b}$$

$$S_i^{\pm}\Psi_{S_iM_i}=[S_i(S_i+1)-M_i(M_i+1)]^{1/2}\Psi_{S_iM_i\pm1}. \tag{5c}$$

In order to obtain the eigenfunction for the unperturbed Hamiltonian $\mathcal{H}_0$, we shall define the total angular momentum $\mathbf{S}=\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3$ and take the following linear combination of the products of $\Psi_{S_iM_i}$:

$$\varphi_{S,M}=\sum_{M_1M_2M_3} c(S,M:M_1,M_2,M_3)\Psi_{S_1M_1}\Psi_{S_2M_2}\Psi_{S_3M_3}. \tag{6}$$

If the coefficients $c(S,M:M_1,M_2,M_3)$ could be so chosen that each $\varphi_{S,M}$ satisfies the relations

$$\mathbf{S}^2\varphi_{S,M}=S(S+1)\varphi_{S,M}, \tag{7a}$$

$$S_z\varphi_{S,M}=M\varphi_{S,M}, \tag{7b}$$

$$S^{\pm}\varphi_{S,M}=[S(S+1)-M(M\pm1)]^{1/2}\varphi_{S,M\pm1}, \tag{7c}$$

it is evident that such $\varphi_{S,M}$'s form a set of eigenfunctions for the present system.

---

[13] H. A. Jahn, Proc. Roy. Soc. (London) **164**, 117 (1937).

We can find in standard references[14] the method for obtaining a complete set of eigenfunctions $\chi_{S',M'}$ for the vector resultant $\mathbf{S}'=\mathbf{S}_1+\mathbf{S}_2$ of our two spin angular momenta $\mathbf{S}_1$ and $\mathbf{S}_2$. Eigenfunctions of this set are the following:

$$\begin{array}{llll} \chi_{3,\pm3}, & \chi_{3,\pm2}, & \chi_{3,\pm1}, & \chi_{3,0}, \\ \chi_{2,\pm2}, & \chi_{2,\pm1}, & \chi_{2,0}, & \\ \chi_{1,\pm1}, & \chi_{1,0}, & \chi_{0,0}. & \end{array} \tag{8}$$

Each one of them is the following linear combination:

$$\chi_{S',M'}=\sum_{M_1M_2} c(S',M':M_1,M_2)\Psi_{S_1,M_1}\Psi_{S_2,M_2} \tag{9}$$

and the coefficients c are uniquely determined.

In a similar way, the eigenfunctions $\varphi_{S,M}$ for the resultant $\mathbf{S}=\mathbf{S}'+\mathbf{S}_3$ can be obtained as linear combinations of the products of $\chi_{S',M'}$ and Ψ_{S_3,M_3}. The coefficients $c(S,M:M_1,M_2,M_3)$ are determined in the usual way. There are sixty-four eigenfunctions[15] in all. These fall into five groups characterized by the same value of S which are denoted in a distinguishable way as $\varphi_{S,M}$, $\varphi'_{S,M}$, $\cdots$, etc. The eigenvalues of $\mathcal{H}_0$ depend only on the value of S, and so we have $n\times(2S+1)$-fold degeneracy for a specified value of S (cf. Fig. 2).

In order to check the correctness of our eigenfunctions, we may calculate the eigenvalues of the Hamiltonian (1) and compare them with those listed in Fig. 2. For example, the nonvanishing matrix elements of the perturbation $J_1\mathbf{S}_2\cdot\mathbf{S}_3$ in the subspace $S=\frac{1}{2}$ spanned by $\varphi'_{\frac{1}{2},\pm\frac{1}{2}}$, $\varphi''_{\frac{1}{2},\pm\frac{1}{2}}$ are given by

$$\begin{aligned} \langle\varphi''_{\frac{1}{2},\pm\frac{1}{2}}|\mathbf{S}_2\cdot\mathbf{S}_3|\varphi''_{\frac{1}{2},\pm\frac{1}{2}}\rangle&=-5/4, \\ \langle\varphi'_{\frac{1}{2},\pm\frac{1}{2}}|\mathbf{S}_2\cdot\mathbf{S}_3|\varphi'_{\frac{1}{2},\pm\frac{1}{2}}\rangle&=-9/4, \\ \langle\varphi'_{\frac{1}{2},\pm\frac{1}{2}}|\mathbf{S}_2\cdot\mathbf{S}_3|\varphi''_{\frac{1}{2},\pm\frac{1}{2}}\rangle&=\tfrac{1}{2}\sqrt{3}. \end{aligned} \tag{10}$$

Therefore, the fourfold degenerate state splits into the following two Kramers doublets:

$$\begin{aligned} \phi_1^{\pm}(\tfrac{1}{2})&=\tfrac{1}{2}[\varphi'_{\frac{1}{2},\pm\frac{1}{2}}+3^{1/2}\varphi''_{\frac{1}{2},\pm\frac{1}{2}}], \quad (\epsilon=-3J_1/4) \\ \phi_2^{\pm}(\tfrac{1}{2})&=\tfrac{1}{2}[3^{1/2}\varphi'_{\frac{1}{2},\pm\frac{1}{2}}-\varphi''_{\frac{1}{2},\pm\frac{1}{2}}], \quad (\epsilon=-11J_1/4). \end{aligned} \tag{11}$$

If $J_1>0$, these two Kramers doublets coincide with the lowest pair in column (a) of Fig. 2 when shifted by an amount $15J_1/4(=S_i(S_i+1)J_1)$. Thus we see that for states of total spin $S=\frac{1}{2}$ the quantum mechanical perturbation procedure yields the same results as are obtained with the vector model. One can extend this calculation to states of total spin $S=\frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$ obtaining in each case similar agreement. The splittings are as shown in Fig. 2(a).

3. SPLITTING DUE TO CRYSTALLINE FIELD

We shall now outline the calculation of the effect of an axial crystalline field on each Cr^{3+} in a cluster. The Hamiltonian (4b) is treated as a perturbation on the unperturbed Hamiltonian (4a). Equation (4b) is written using spin components with respect to microscopic principal axes. Transformation of (4b) to the common coordinate axes shown in Fig. 3 gives the following:

$$\mathcal{H}'=\tfrac{1}{4}\sum_{i=1}^{3} D_i[(S_i^+S_i^-+S_i^-S_i^+)+C_iS_i^{+2}+C_i^*S_i^{-2}], \tag{12}$$

where $C_1=C_2^*=\frac{1}{2}[1-3^{1/2}i]$, $C_3=-1$. In the following, we shall proceed by taking $D_i\equiv D$ as explained in Sec. 1.

In the calculation of the matrix elements of $\mathcal{H}'$, the following relations are useful in addition to the fact that $\mathcal{H}'$ is Hermitian with respect to the unperturbed eigenfunctions:

$$\langle\varphi_{S,M}|S_i^+S_i^-|\varphi_{S,M}\rangle=\langle\varphi_{S,-M}|S_i^-S_i^+|\varphi_{S,-M}\rangle, \tag{13a}$$

or

$$\langle\varphi_{S,M}|\mathcal{H}'|\varphi_{S,M}\rangle=\langle\varphi_{S,-M}|\mathcal{H}'|\varphi_{S,-M}\rangle, \tag{13b}$$

etc.

and

$$\langle\varphi_{S,M}|\mathcal{H}'|\varphi'_{S,M}\rangle=\langle\varphi_{S,-M}|\mathcal{H}'|\varphi'_{S,-M}\rangle, \tag{13c}$$

$$\langle\varphi_{S,M}|\mathcal{H}'|\varphi_{S,M'}\rangle=\langle\varphi_{S,-M}|\mathcal{H}'|\varphi_{S,-M'}\rangle^*, \tag{13d}$$

$$\langle\varphi_{S,M}|\mathcal{H}'|\varphi'_{S,M'}\rangle=\langle\varphi_{S,-M}|\mathcal{H}'|\varphi'_{S,-M'}\rangle^*, \tag{13e}$$

etc.

$$M'=M\pm2.$$

It will be evident that we have nonvanishing matrix elements only within the subspace of the same S value. Therefore, we can set up separately the secular equations according to the values of S.

In the case of $S=\frac{1}{2}$, the perturbation Hamiltonian has only diagonal elements and these all equal $15D/4$. The fourfold degeneracy still remains, and $\varphi'_{\frac{1}{2},\pm\frac{1}{2}}$ and $\varphi''_{\frac{1}{2},\pm\frac{1}{2}}$ are also eigenfunctions in the perturbed system.

The calculations for higher total spin S, are straightforward but tedious. One finds for $S=\frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$, respectively, eight, nine, eight, and five separate Kramers doublets. These eigenvalues have been calculated[15] and

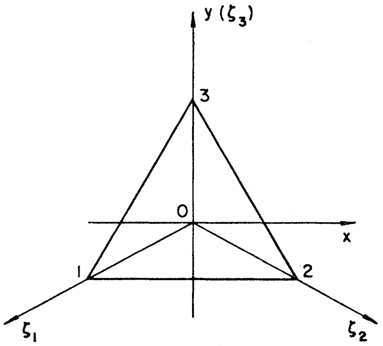

FIG. 3. Coordinate axes of a cluster (x,y,z) and microscopic coordinate axes (ξ_i,η_i,ζ_i). The ξ_i axis is taken in the direction of the z axis.

---

[14] See, for instance, E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).

[15] These are given in an expanded version of the present paper issued as Tech. Rept. No. 1, for contract Nonr-760(26)NR018-301, 1 July 1965.

are shown in column b of Fig. 2. The eigenvalue of the ith Kramers doublet belonging to $S=\frac{3}{2}$, shifted downward by $15D/4$, is labeled E_i. The symbols E_i', E_i'', and E_i''' designate, similarly, doublets belonging to $S=\frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$, respectively.

4. COMPARISON WITH EXPERIMENT

The paramagnetic susceptibility χ_z has been computed for the Hamiltonian

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}'+g\mu_B S_z H\,, \qquad (14)$$

where the magnetic field H is applied along the z axis. This is most easily done using Van Vleck's formula[16] which is simplified in this case since the matrix elements of S_z between states of different S vanish, e.g., $S_z(SM\colon S+1M)=0$. The calculations of χ_x and χ_y have also been performed and like that of χ_z are straightforward[15] but lengthy.

Measurements of the susceptibility[11,17] have been made only on powdered samples and so comparison will be made with the following expression for χ_p, the average of χ_x, χ_y, and χ_z:

$$\chi_p=\frac{Ng^2\mu_B{}^2}{6kT}\times\frac{1.5A_0+7.5A_1\exp(-1.5J_0/kT)+17.5A_2\exp(-4J_0kT)+31.5A_3\exp(-7.5J_0/kT)+49.5A_4\exp(-12J_0/kT)}{A_0+A_1\exp(-1.5J_0/kT)+A_2\exp(-4J_0/kT)+A_3\exp(-7.5J_0/kT)+A_4\exp(-12J_0/kT)}, \qquad (15)$$

where

$$A_0=2\,,\quad A_1=\sum_{i=1}^{8}\exp\left(\frac{-E_i}{kT}\right),\quad A_2=\sum_{i=1}^{9}\exp\left(\frac{-E_i'}{kT}\right),\quad A_3=\sum_{i=1}^{8}\exp\left(\frac{-E_i''}{kT}\right),\quad A_4=\sum_{i=1}^{5}\exp\left(\frac{-E_i'''}{kT}\right). \qquad (16)$$

In view of the fact that the value of D in most hydrated chromic salts is of the order of 10^{-1} cm^{-1},[18] we have looked for the most reasonable values of J_0 and D by means of the computer for D values ranging from $0.05k$ to $0.14k$ (in steps of $0.01k$) and J_0 values from $24k$ to $34k$ (in steps of $2k$). The values of D in this range, however, have scarcely any influence upon the value of χ_p. Closest agreement can be obtained with $J_0=30k$ below hydrogen temperatures as suggested by Wucher and Gijsman, and with $J_0=32k$ at higher temperatures. If we assume a much larger value of D, i.e., $D\sim 1k$, the crystalline field begins to affect the calculated values of χ_p and much better agreement can be achieved. At present, however, there appears to be no reason to assume the value of D in this compound to be larger by an order of magnitude than that found in other Cr^{3+} salts.

The most significant discrepancy with experiment is found, however, when one attempts to fit specific heat data for $[Cr_3(CH_3COO)_6(OH)_2]Cl\cdot 8H_2O$ with this model. In order to discuss the helium-temperature data of Wucher and Wasscher,[10] it is sufficient to consider only the lowest states ($S=\frac{1}{2}$) and the next group of excited states ($S=\frac{3}{2}$). As was shown in Sec. 3, the lowest state remains fourfold degenerate even when the effect of an axial crystalline field is included. The calculated specific heat then shows a gradual rise with increasing temperature in the helium range with no indication of the plateau near 2°K found experimentally (Fig. 4).

A very large value of D shifts the lowest Kramers doublet belonging to the $S=\frac{3}{2}$ group close to the ground state, causing the calculated specific heat to exhibit a Schottky anomaly. The height of this anomaly, however, is too small to fit the data. It appears quite likely

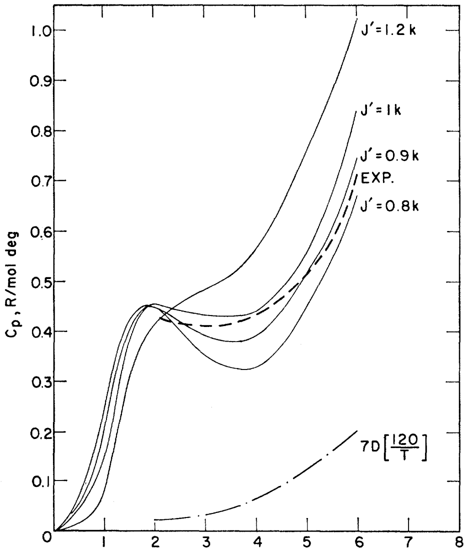

FIG. 4. Specific heat curves calculated for $J_0=30k$ and values of J' shown in the figure. Dashed line shows the measurements. The calculation includes the lattice specific heat which is given by the Debye functions D shown by a dashed dotted line (after Wucher and Wasscher).

---

[16] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, England, 1932), Chap. VII.

[17] J. T. Schriempf and S. A. Friedberg, J. Chem. Phys. **40**, 296 (1964).

[18] K. D. Bowers and J. Owen, Rept. Progr. Phys. **18**, 304 (1955); C. F. Davis and M. W. P. Strandberg, Phys. Rev. **105**, 447 (1957).

that only by invoking a mechanism which lifts at least partially the fourfold degeneracy of the ground state ($S=\frac{1}{2}$) can we explain the low-temperature specific heat of $[\mathrm{Cr_3(CH_3COO)_6(OH)_2}]\mathrm{Cl\cdot 8H_2O}$. In the following section we examine mechanisms which do this while preserving the assumed symmetry of the cluster of three $\mathrm{Cr^{3+}}$ ions.

5. HIGHER ORDER SPIN COUPLING

Let us consider first the effect of intercluster interaction of dipolar or exchange character. Extending the results of Van Vleck,[19] for interacting ions, one expects this effect to produce extra terms in the specific heat in addition to the Schottky anomaly which reflects the energy-level scheme of a cluster. Such interaction would also affect the magnetic susceptibilities producing departures from Curie's law at temperatures such that kT is of the order of the interaction energy. Measurements[17] down to 0.5°K, however, yield a Weiss constant of ~0.1°K indicating that intercluster interaction is too small to account for the specific heat observations. This conclusion is consistent with structural evidence mentioned above.

Tentative calculation shows that we may get a reasonable temperature dependence of the calculated specific heat if the lowest quartet splits into two Kramers doublets with a separation of several degrees. Dipolar interaction among the three spins in a cluster can remove this degeneracy, but it is too small (order of less than $0.1k$). An anisotropic exchange interaction can also split the lowest state. This is roughly of the order of $\sim J_0(g-2)^2$, and is also expected to be negligibly small in the present case because the estimated g factor is very close to 2.

Another possible exchange interaction which can give rise to a splitting of the lowest levels will be a higher order spin coupling among the three spins. An interaction of this kind may be derived in a way analogous to that giving the familiar pseudodipolar interaction. In a crystalline field of cubic or axial symmetry, the $\mathrm{Cr^{3+}}$ ion is in a singlet A_2 ground state which is expressed by $\psi_0\sim xyz$. This ground state as well as the excited T_2 states $\psi_1\sim x(y^2-z^2)$, $\psi_2\sim y(z^2-x^2)$, $\psi_3\sim z(x^2-y^2)$ are able to overlap appreciably with π orbitals of the acetate bridges, two of which link each $\mathrm{Cr^{3+}}$ ion to its two neighbors in a cluster. The result will be π conjugation throughout the cluster of three $\mathrm{Cr^{3+}}$ ions. This situation resembles in some ways the π conjugation found in trivalent transition metal complexes of acetylacetone.[20] When three interacting ions are considered, the number of orbital states becomes 7^3, each with a degeneracy in the spin of 64. In a satisfactory approximation, it will be enough to consider the lowest and the first excited orbital states. The lowest state we denote by $A_2(1)A_2(2)A_2(3)$, showing that the wave function is the product of the individual wave functions A_2 for the ions 1, 2, and 3. The next higher states, lying at ΔE, have wave functions $T_2(1)A_2(2)A_2(3)$, $A_2(1)T_2(2)A_2(3)$, and $A_2(1)A_2(2)T_2(3)$, where $T_2(i)$ denotes one of the wave functions belonging to the T_2 state of ith ion.

In the present system, the Hamiltonian should be symmetric with respect to permutation of the three spins $\mathbf{S}_1$, $\mathbf{S}_2$, and $\mathbf{S}_3$. The third-order term, for instance, of the form

$$S_1^xS_2^xS_3^x+S_1^yS_2^yS_3^y+S_1^zS_2^zS_3^z \tag{17}$$

might be expected to appear when the spin-orbit coupling in the individual ions is treated as a perturbation. It has the required symmetry. However, this type of Hamiltonian is not invariant under time reversal and would give rise to a spontaneous magnetization. It may, therefore, be excluded. One of the terms of the third-order perturbation energy which includes exchange interaction as well as spin-orbit coupling is given by

$$\begin{aligned}(\lambda/\Delta E)^2&\langle A_2(1)A_2(2)A_2(3)|\mathbf{L}_1\cdot\mathbf{S}_1|T_2(1)A_2(2)A_2(3)\rangle\\ &\times\langle T_2(1)A_2(2)A_2(3)|J\mathbf{S}_2\cdot\mathbf{S}_3|T_2(1)A_2(2)A_2(3)\rangle\\ &\times\langle T_2(1)A_2(2)A_2(3)|\mathbf{L}_1\cdot\mathbf{S}_1|A_2(1)A_2(2)A_2(3)\rangle.\end{aligned} \tag{18}$$

The spin Hamiltonian obtained from this kind of procedure may be written in the following form, as can be seen from a symmetry argument

$$\begin{aligned}\mathcal{H}''=J'[(\mathbf{S}_1\cdot\mathbf{S}_2)(\mathbf{S}_2\cdot\mathbf{S}_3)&+(\mathbf{S}_1\cdot\mathbf{S}_3)(\mathbf{S}_3\cdot\mathbf{S}_2)\\ &+(\mathbf{S}_3\cdot\mathbf{S}_1)(\mathbf{S}_1\cdot\mathbf{S}_2)].\end{aligned} \tag{19}$$

The so-called biquadratic exchange interaction[21] between two spins may be obtained by a similar procedure in which we consider terms of the following form:

$$\begin{aligned}(\lambda/\Delta E)^2&\langle A_2(1)A_2(2)A_2(3)|\mathbf{L}_1\cdot\mathbf{S}_1|T_2(1)A_2(2)A_2(3)\rangle\\ &\times\langle T_2(1)A_2(2)A_2(3)|J\mathbf{S}_1\cdot\mathbf{S}_2|A_2(1)T_2(2)A_2(3)\rangle\\ &\times\langle A_2(1)T_2(2)A_2(3)|\mathbf{L}_2\cdot\mathbf{S}_2|A_2(1)A_2(2)A_2(3)\rangle.\end{aligned}$$

The diagonal matrix elements of the exchange energy in (18) can be expected to have an appreciably larger value than the off-diagonal elements such as the above term. Thus, we may expect the interaction given in Eq. (19) to be more important than the biquadratic exchange interactions. In the following, we shall consider the Hamiltonian $\mathcal{H}''$, neglecting crystalline field effects.

6. SPLITTING DUE TO HIGHER ORDER SPIN COUPLING

The Hamiltonian $\mathcal{H}''$ has no matrix elements between states having different values of S. We can, therefore, solve the perturbation problem in the subspace of given S as was done in Sec. 3. The eigenfunctions and eigenvalues of the perturbed system have been calculated[15] taking as unperturbed eigenfunctions those of $\mathcal{H}_0$ (4a). The energies of the perturbed levels relative

---

[19] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

[20] H. S. Jarrett, J. Chem. Phys. **27**, 1298 (1957).

[21] P. W. Anderson, Solid State Phys. **14**, 99 (1963).

to the eigenvalues of $\mathcal{H}_0$ may be summarized as follows:

$S=\frac{1}{2}$: splits into two Kramers doublets,
$\epsilon_1{}^0=(123-24\sqrt{3})J'/16$ and
$\epsilon_2{}^0=(123+24\sqrt{3})J'/16$;
$S=\frac{3}{2}$: splits into four fourfold degenerate states,
$\epsilon_1=-11.6194J'$, $\epsilon_2=-5.3576J'$,
$\epsilon_3=-0.9014J'$, $\epsilon_4=5.1284J'$;
$S=\frac{5}{2}$: splits into three sixfold degenerate states,
$\epsilon_1'=-14.6678J'$, $\epsilon_2'=-4.3325J'$,
$\epsilon_3'=1.5627J'$;
$S=\frac{7}{2}$: splits into two eightfold degenerate states,
$\epsilon_1''=(-27/16+27\sqrt{3}/8)J'$,
$\epsilon_2''=(-27/16-27\sqrt{3}/8)J'$;
$S=\frac{9}{2}$: tenfold degeneracy remains but level shifted
$\epsilon'''=(9/4)^2 3J'$.

These splittings are shown in column *c* of Fig. 2.

7. ESTIMATION OF NUMERICAL VALUES OF PARAMETERS

Having obtained the eigenvalues and the eigenfunctions, the expression for the powder susceptibility can be again obtained in the same form as Eq. (15) provided the following substitutions are made.

$$
\begin{gathered}
A_0=\sum_{i=1}^{2}\exp\left(\frac{-\epsilon_i{}^0}{kT}\right),\\
E_1=E_2=\epsilon_1,\quad E_3=E_4=\epsilon_2,\quad E_5=E_6=\epsilon_3,\\
E_7=E_8=\epsilon_4,\\
E_1'=E_2'=E_3'=\epsilon_1',\quad E_4'=E_5'=E_6'=\epsilon_2',\\
E_7'=E_8'=E_9'=\epsilon_3',\\
E_i''=\epsilon_1''(i=1,2,3,4),\quad E_j''=\epsilon_2''(j=5,6,7,8),\\
E_k'''=(9/4)^2 3J'.
\end{gathered}
\tag{20}
$$

We have looked for the most reasonable values of J_0 and J' for J' in the range $0.2k$ to $1.3k$ (in steps of $0.1k$) and J_0 assuming the values $28k$, $30k$, and $32k$. Some results of the calculations are shown in Fig. 5. Good agreement is obtained with $J_0=32k$, $J'=0.40$ or $J_0=30k$, $J'=0.20k$.

The formula for the magnetic specific heat in the helium temperature region is conveniently written as

$$C=\frac{N}{kT^2}\left[\frac{F''}{F}-\left(\frac{F'}{F}\right)^2\right],\tag{21}$$

where

$$F=1+\exp(-\delta/kT)+2\alpha\exp(-\Delta/kT),\tag{22a}$$

$$F'=\delta\exp(-\delta/kT)+2[\Delta\cdot\alpha+\beta]\exp(-\Delta/kT),\tag{22b}$$

$$F''=\delta^2\exp(-\delta/kT)+2[\Delta^2\cdot\alpha+2\Delta\cdot\beta+\gamma]\exp(-\Delta/kT),\tag{22c}$$

$$\alpha=1+\exp(-\delta_1'/kT)+\exp(-\delta_2'/kT)+\exp(-\delta_3'/kT),\tag{23a}$$

$$\beta=\delta_1'\exp(-\delta_1'/kT)+\delta_2'\exp(-\delta_2'/kT)+\delta_3'\exp(-\delta_3'/kT),\tag{23b}$$

$$\gamma=\delta_1'^2\exp(-\delta_1'/kT)+\delta_2'^2\exp(-\delta_2'/kT)+\delta_3'^2\exp(-\delta_3'/kT),\tag{23c}$$

and

$$
\begin{gathered}
\delta=\epsilon_2{}^0-\epsilon_1{}^0,\\
\delta_i'=\epsilon_{i+1}-\epsilon_i,\\
\Delta=1.5J_0+\epsilon_1-\epsilon_1{}^0.
\end{gathered}
\tag{24}
$$

The results of the calculation are shown in Fig. 4. For the lattice part of the specific heat, we took the values estimated by Wucher and Wasscher. A reasonably good fit of the data can be obtained with $J_0=30k$ and $J'=0.9k$. It is interesting to note that the fit obtained with this theory is significantly better than that got with the simple Kambe model. Comparing the values of J' required to fit the susceptibility and low-temperature specific heat, there is perhaps reason to suppose that J' is temperature dependent in the opposite sense to J_1 of the simple theory. Regarded as a purely phenomenological procedure, the introduction of the higher order spin coupling [Eq. (19)] appears somewhat more successful than the assumption of an unsymmetrical cluster made in the Kambe theory. Whether a coefficient J' of the required magnitude is physically reasonable is a question we shall consider in the concluding discussion.

8. ORDERED SPIN ARRANGEMENT IN A CLUSTER

We shall consider in this section the ordered spin arrangement in the present three spin system. The measurement of susceptibility or specific heat does not show any evidence of cooperative phenomena at least down to 0.4°K. Thus we do not expect long-range order

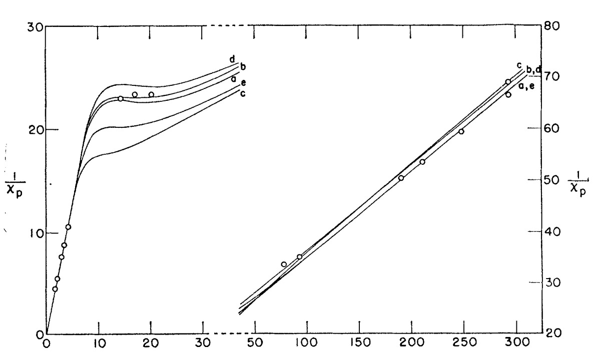

FIG. 5. Several examples of the calculation of reciprocal susceptibility. The chosen parameters are: (a) $J_0=30k$, $J'=0.2k$, (b) $J_0=32k$, $J'=0.4k$, (c) $J_0=32k$, $J'=1.2k$, (d) $J_0=32k$, $J'=0.2k$, (e) $J_0=30k$, $J'=0.6k$. The small circles are the experimental points (after Wucher and Gijsman).

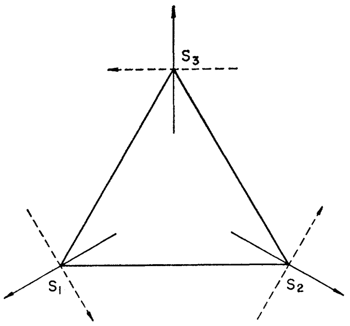

FIG. 6. Spin arrangement in a cluster. Solid (dashed) arrows show the arrangement in the case D is negative (positive).

in the crystal due to intercluster interaction to appear above that temperature. However, the cluster itself should exhibit some definite spin arrangement because of the rather large intracluster exchange interaction.

First, we shall only treat the exchange Hamiltonian for two-spin interactions

$$\mathcal{H}_0 = J_0(\mathbf{S}_1\cdot\mathbf{S}_2+\mathbf{S}_2\cdot\mathbf{S}_3+\mathbf{S}_3\cdot\mathbf{S}_1)\,.$$

As an approximation, we shall consider the spins $\mathbf{S}_i$ as classical vectors and define the nine-dimensional vector $\mathbf{e}$ whose components are

$$\begin{aligned}(e_1,e_2,e_3)&=(S_{1x},S_{1y},S_{1z})\,,\\(e_4,e_5,e_6)&=(S_{2x},S_{2y},S_{2z})\,,\\(e_7,e_8,e_9)&=(S_{3x},S_{3y},S_{3z})\,.\end{aligned}\qquad(25)$$

Then, the cluster Hamiltonian can be written in a quadratic form with respect to e_i's, where we have a condition of constraint $\sum e_i^2=\text{const}$. If we write the energy as $\frac{1}{2}\sum A_{ij}e_ie_j$, the problem of finding the lowest energy state can be reduced to the eigenvalue problem[22] of a matrix $[A_{ij}]$. The 9×9 matrix $[A_{ij}]$ can be reduced to three 3×3 submatrices

$$\begin{bmatrix}0&1&1\\1&0&1\\1&1&0\end{bmatrix}\qquad(26)$$

with the appropriate transformation matrix. The lowest eigenvalue, $\epsilon=-1$, is doubly degenerate and the eigenvectors, which are orthogonal to each other, are the ones which satisfy the condition,

$$\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3=0\,.\qquad(27)$$

This implies a coplanar arrangement of three spins. One possibility is shown in Fig. 6. Another spin arrangement which corresponds to a higher eigenvalue $\epsilon=2$ is the one in which all three spins are parallel. The effect of the crystalline field considered in Sec. 3 may stabilize either arrangement in Fig. 6 depending on the sign of D.

Next, we shall discuss the effect of a three-spin interaction

$$\mathcal{H}''=J'[(\mathbf{S}_1\cdot\mathbf{S}_2)(\mathbf{S}_2\cdot\mathbf{S}_3)+(\mathbf{S}_2\cdot\mathbf{S}_3)(\mathbf{S}_3\cdot\mathbf{S}_1)+(\mathbf{S}_3\cdot\mathbf{S}_1)(\mathbf{S}_1\cdot\mathbf{S}_2)]\,.$$

We shall denote by θ_1 and θ_2 the angles between spin vectors $\mathbf{S}_1$ and $\mathbf{S}_2$, and $\mathbf{S}_2$ and $\mathbf{S}_3$, respectively. For the fixed angles θ_1 and θ_2, the spin vectors $\mathbf{S}_1$ and $\mathbf{S}_3$ lie on the conical surfaces which make angles θ_1 and θ_2, respectively, with the vertical axis in the direction of $\mathbf{S}_2$, and the first term is constant. We shall take the vertical axis as the polar axis, and denote the azimuthal angle of the spin vector $\mathbf{S}_3$ by ψ which is measured from the plane of $\mathbf{S}_1$ and $\mathbf{S}_2$. Then our problem is to minimize the following with respect to θ_1, θ_2, and ψ:

$$\begin{aligned}F(\theta_1,\theta_2,\psi)=J_0[&\cos\theta_1+\cos\theta_2+\sin\theta_1\sin\theta_2\cos\psi\\&+\cos\theta_1\cos\theta_2]+J'\{\cos\theta_1\cos\theta_2+(\cos\theta_1+\cos\theta_2)\\&\times[\sin\theta_1\sin\theta_2\cos\psi+\cos\theta_1\cos\theta_2]\}\,.\end{aligned}\qquad(28)$$

If we use the numerical values of J_0 and J' to exclude impossible solutions, the values of θ_1, θ_2, and ψ which minimize $F(\theta_1,\theta_2,\psi)$ can be obtained as the roots of the following set of simultaneous equations:

$$\begin{aligned}\sin\theta_1\sin\theta_2\sin\psi&=0\,,\\\sin\tfrac{1}{2}(\theta_1+\theta_2)\cdot f_1(\theta_1,\theta_2,\psi)&=0\,,\\\sin\tfrac{1}{2}(\theta_1-\theta_2)\cdot f_2(\theta_1,\theta_2,\psi)&=0\,,\end{aligned}\qquad(29)$$

where

$$\begin{aligned}f_1(\theta_1,\theta_2,\psi)=\cos\tfrac{1}{2}(\theta_1+\theta_2)\{&(\cos\psi-1)\\\times[J_0+J'(\cos\theta_1+\cos\theta_2)]-J'\}&-\cos\tfrac{1}{2}(\theta_1-\theta_2)\\\times[J_0+J'(\sin\theta_1\sin\theta_2\cos\psi&+\cos\theta_1\cos\theta_2)]\,,\end{aligned}\qquad(30a)$$

$$\begin{aligned}f_2(\theta_1,\theta_2,\psi)=\cos\tfrac{1}{2}(\theta_1-\theta_2)\{&(\cos\psi+1)\\\times[J_0+J'(\cos\theta_1+\cos\theta_2)]+J'\}&+\cos\tfrac{1}{2}(\theta_1+\theta_2)\\\times[J_0+J'(\sin\theta_1\sin\theta_2\cos\psi&+\cos\theta_1\cos\theta_2)]\,.\end{aligned}\qquad(30b)$$

From the simultaneous equations

$$\sin\theta_1=0\ (\text{or}\ \sin\theta_2=0),\ \sin\tfrac{1}{2}(\theta_1\pm\theta_2)=0:$$

the following solution can be obtained easily

(i) $\theta_1=\theta_2=0$, or $\theta_1=\theta_2=\pi$.

The other sets of simultaneous equations give the following solutions:

(ii) $\sin\psi=0$, $\sin\frac{1}{2}(\theta_1+\theta_2)=0$, $f_2(\theta_1,\theta_2,\psi)=0$;

$$\psi=0\,,\quad\theta_1=-\theta_2=\cos^{-1}(-\tfrac{1}{2})\,,$$

(iii) $\sin\psi=0$, $\sin\frac{1}{2}(\theta_1-\theta_2)=0$, $f_1(\theta_1,\theta_2,\psi)=0$;

$$\psi=\pi\,,\quad\theta_1=\theta_2=\cos^{-1}(-\tfrac{1}{2})\,,$$

(iv) $\sin\theta_1=0\,(\sin\theta_2=0)$, $f_1(\theta_1,\theta_2,\psi)=f_2(\theta_1,\theta_2,\psi)=0$;

$$\theta_1=0\,,\quad\theta_2=\pi\quad(\theta_1=\pi,\theta_2=0)\,,$$

or

$$\psi=\pi/2\,,\quad\theta_1=\pi\,,\quad\theta_2=\pi/2\quad(\theta_1=\pi/2,\theta_2=\pi)\,,$$

---

[22] J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946); N. Uryû, *ibid.* **136**, A527 (1964).

$$\text{(v)}\qquad \sin\psi=0,\quad f_1(\theta_1,\theta_2,\psi)=f_2(\theta_1,\theta_2,\psi)=0;$$

$$\psi=0 \quad\text{or}\quad \pi$$

and

$$\theta_1=0,\quad \theta_2=\pm\pi \quad\text{or}\quad \theta_1=\pm\pi,\quad \theta_2=0.$$

The last set of equations can be solved by seeking the points of intersection of two curves $f_1(u,v)=0$ and $f_2(u,v)=0$ in the u-v plane, where we have made a transformation $u=\cos[\frac{1}{2}(\theta_1+\theta_2)]$ $v=\cos[\frac{1}{2}(\theta_1-\theta_2)]$. The only possible solution is $u=v=0$ for the present values of J_0 and J' and thus we get the above solution. The solutions (ii) and (iii) are identical, and this solution turns out to correspond to the lowest energy state. Therefore, the spin arrangement of the lowest energy is again the one shown in Fig. 6.

9. CONCLUSION

In the preceding sections of this paper we have explored the possibility of explaining the observed magnetic and thermal properties of $[Cr_3(CH_3COO)_6(OH)_2]Cl\cdot 8H_2O$ without requiring that the clusters of three Cr^{3+} ions have less than trigonal symmetry. If the ions in a cluster are coupled only by isotropic antiferromagnetic exchange interaction, the assumption of symmetry leads to a ground state of total spin $S=\frac{1}{2}$ which consists of two degenerate Kramers doublets. Removal of this degeneracy is essential if the theory is to reproduce the data, especially the low-temperature heat-capacity observations. This is illustrated in the calculation of the effect of adding an axial component to the cubic crystalline field at each Cr^{3+} ion. The presence of such a perturbation is readily inferred from the structure of the solid. Allowing the coefficient D to assume unusually large values, it proves possible to fit the susceptibility data. The specific heat, however, cannot be described adequately simply because the axial fields leave unaffected the fourfold ground-state degeneracy of a cluster.

Within the requirement of a symmetric cluster, the most reasonable explanation of the necessary splitting of the ground state into two Kramers doublets has been found in a novel type of higher order spin coupling. As a phenomenological expedient, the introduction of this three-body interaction actually appears somewhat more successful in fitting the observations than does relaxation of the requirement of a symmetrical cluster. Its physical plausibility, however, is difficult to assess.

In deriving an interaction of suitable form we have been guided primarily by symmetry arguments and the assumption of the existence of π orbitals which enable electrons to circulate among the three ions. At first sight this coupling might be estimated to be of the same order of magnitude as the anisotropic exchange interaction between pairs of ions and thus to be negligibly small. However, it should be noted that the establishment of strong π conjugation in the present three-spin system will give rise to a rather different situation from that usually found for exchange interactions modified by spin-orbit coupling. A crude argument suggesting that J' may have the required magnitude can be given as follows: The superexchange integral J_0 between neighboring magnetic ions can be considered to correspond to b^2J/U^2 with J the exchange constant appearing in (43), b a transfer integral, and U an average excitation energy.[23] Taking J_0 to be $\sim 30k$ and $(b/U)^2$ to have a reasonable value of $\sim 10^{-3}$, we find $J\sim 10^4k$. Since ΔE, the separation of orbital ground and excited states, is $\sim 10^4k$ and λ, the spin-orbit coupling constant, is $\sim 10^2k$, then $J'\sim(\lambda/\Delta E)^2J$ is estimated to be $\sim 1k$ as required. Without detailed knowledge of the behavior of the π electrons in a cluster or of the role of the common $O^{=}$ ion in its center, further attempts to refine this estimate would probably not be fruitful. It suggests, however, that higher order spin coupling of this type may be large enough to separate the two Kramers doublets comprising the cluster ground state by the required amount.

As was emphasized in the introduction, in spite of the absence of pronounced cluster distortion in the room-temperature x-ray structural evidence, departure from trigonal symmetry may still account at low temperatures for the major part of the ground state splitting. Even in that event, however, if our estimate of magnitude is meaningful, the contribution of higher order spin coupling to the doublet separation may not be completely negligible.

In the temperature range covered by the experiments performed to date on compounds containing clusters of three paramagnetic ions, no direct evidence of the onset of cooperative long range spin order has been seen. These clusters have magnetic ground states, however, and at sufficiently low temperatures intercluster interaction must eventually cause such cooperative effects to occur. Thus for $[Cr_3(CH_3COO)_6(OH)_2]Cl\cdot 8H_2O$, experiments below ~0.1°K should yield useful information about intercluster coupling and perhaps further hints as to the nature of intracluster interaction as well. It may also be possible to study at higher temperatures the ordered spin arrangement within a cluster. This would provide perhaps more direct evidence about the intracluster couplings.

ACKNOWLEDGMENTS

We should like to express our sincere appreciation to Dr. S. C. Chang and Professor G. A. Jeffrey for communicating to us prior to publication the results of their x-ray structural studies and permitting us to quote from them at length. We also wish to thank Dr. G. Wagner, R. Revay, and M. Amitay for their valuable assistance in the performance of numerical calculations with the Bendix G-20 computer. Helpful comments by Professor R. E. Cutkosky are very much appreciated.

---

[23] J. H. Van Vleck, J. Phys. Radium 12, 262 (1951).