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The Effect of Crystalline Electric Fields on the Paramagnetic Susceptibility of Cupric Salts

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The paramagnetic susceptibility of the cupric ion in the hexahydrate sulphates $Cu(NH_4)_2(SO_4)_2 : 6H_2O$ and $CuK_2(SO_4)_2 : 6H_2O$ has been computed on the assumption that the crystalline field has monoclinic symmetry but deviates only slightly from cubic symmetry. The computed variation of the *magnitudes* of the principal susceptibilities with temperature agrees with the data over the limited range of experimental measurements. The mean susceptibility should follow quite closely the simple formula $\chi = A/T + B$, even if the individual susceptibilities do not. This agrees very well with the observations of de Haas and Gorter on the mean susceptibility of $CuSO_4 : 5H_2O$ for the temperature range 14°K to 290°K. In a rhombic field, such as was previously used by Schlapp and Penney for calculations on Co^{++} and Ni^{++}, the directions of the principal magnetic axes are independent of temperature, while the more general monoclinic field gives a rotation of the magnetic axes as the temperature is varied. The calculated variation of the *direction* of the principal axes with temperature in Cu^{++} is in qualitative accord with the observations of Bartlett, but the numerical agreement is not very good. The introduction of an exceedingly asymmetrical diamagnetic correction greatly improves the agreement for the potassium salt, but more likely, the large rotations observed by Bartlett are due to allotropic changes, since the temperature range is not far below the temperatures at which dehydration and decomposition take place. From the choice of parameters which give agreement with the magnetic data, conclusions are drawn about the structures of these crystals.

INTRODUCTION

The paramagnetic susceptibility of the ions of the iron group has recently received considerable theoretical attention. The general theory of the quenching of the magnetic contribution of the orbit by crystalline fields of the Bethe-Kramers type has been outlined by Van Vleck in his recent book,[1] confirming the hypothesis of Stoner and Bose. Detailed calculations have been carried out for Co, Ni and Cr by Schlapp and Penney[2] with very good results. This paper gives the results of calculations on Cu. Schlapp and Penney assumed that the potential field in the crystal could be represented by a predominant field of cubic symmetry upon which was superposed a small field of rhombic symmetry. The axes of the two fields were assumed to coincide so that the resulting field had rhombic symmetry. Our procedure is more general as we assume the axes of the rhombic field to be rotated about the common z-axis through an angle α away from the axes of the cubic field. This gives a resultant field of monoclinic symmetry which agrees better with the crystallographic symmetry, and allows the principal magnetic axes to vary in direction with temperature.

The assumed Hamiltonian is therefore:

$$H = D(x^4+y^4+z^4) + \{Ax'^2 + By'^2 - (A+B)z'^2\} + A'(\mathbf{L}\cdot\mathbf{S}) + \beta\mathfrak{H}\cdot(\mathbf{L}+2\mathbf{S}). \quad (1)$$

The first two terms are respectively the contributions of the cubic and rhombic fields, the respective axes being orientated so that $\cos(x, x') = \cos(y, y') = \cos\alpha$, and $\cos(z, z') = 1$. These two terms will be designated as the cubic and rhombic terms. The third term is the orbit-spin interaction and the last is the Zeeman term due to the external magnetic field $\mathfrak{H}$. Also, β is the Bohr magneton $eh/4\pi mc$, and A' is the orbit-spin coupling coefficient which, according to Laporte,[3] has the value -852 cm^{-1} for Cu^{++}. **L** and

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[1] J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford Press (1932). See especially Chapter XI.

[2] R. Schlapp and W. G. Penney, Phys. Rev. **42**, 666 (1932). For Co, Ni and Cr, as well as for Cu, the affix $^{++}$ is to be understood whenever the ion is mentioned.

[3] O. Laporte, Zeits. f. Physik **47**, 761 (1928). He gives the multiplet separation of the lowest term as 2130 cm^{-1}, which gives A' the value -852 cm^{-1}.

S are angular momentum vectors associated with the quantum numbers L and S of the orbit and spin, which have the values 2 and $\frac{1}{2}$, respectively. The rhombic term of the Hamiltonian may be expressed as follows in terms of the axes of the cubic field and the angle α:

$$(A\cos^2\alpha+B\sin^2\alpha)x^2+(A\sin^2\alpha+B\cos^2\alpha)y^2 \\ -(A+B)z^2+(A-B)xy\sin 2\alpha. \quad (2)$$

We may first consider the problem qualitatively. The cubic field is assumed so large that its effect is predominant. Bethe[4] has shown by group theory, that under the influence of an electric field of cubic symmetry, the fivefold degenerate representation of the orbital rotation group for $L=2$ divides into two irreducible representations Γ_3 and Γ_5 which are respectively doubly and triply degenerate. In order to obtain agreement with experiment it is necessary to assume that the lowest energy level belongs to the representation Γ_3. This also agrees with the conclusions of Van Vleck.[5]

The introduction of the electron spin of course complicates the problem, doubling the number of states. Even after the introduction of the orbit-spin forces many of the states coincide, for a well-known theorem of Kramers tells us that, in a system with an odd number of electrons, there is always at least a twofold degeneracy. Fig. 1 shows how the energy levels arising from a ^2D configuration behave in the presence of the various fields. The right half of the diagram is labelled with Bethe's notation, while on the left the notation corresponds to that of Mulliken.[6] It is particularly to be noted that when the twofold level, Γ_3, is increased to a fourfold one by the introduction of the spin, none of the four components separate until rhombic or magnetic field terms are included. In the language of group theory, $D_{\frac{1}{2}}\times\Gamma_3=\Gamma_8$, where $D_{\frac{1}{2}}$ is the rotation group for the spin, Γ_3 is a doubly degenerate representation of the single-valued cubic group, and Γ_8 is a fourfold degenerate representation of the double-valued cubic group which is characteristic of half-integral quantum numbers.[7] The degeneracy is completely removed only by the simultaneous application of an electric field of rhombic (or monoclinic) symmetry and a magnetic field, the latter removing the Kramers degeneracy. Without the magnetic field, but including the electric field terms, the whole problem has a twofold degeneracy. The components which are due to the magnetic field may be distinguished by the superscripts + or −, while the five levels in the absence of the field are designated by Roman or Arabic numerals without the superscript.

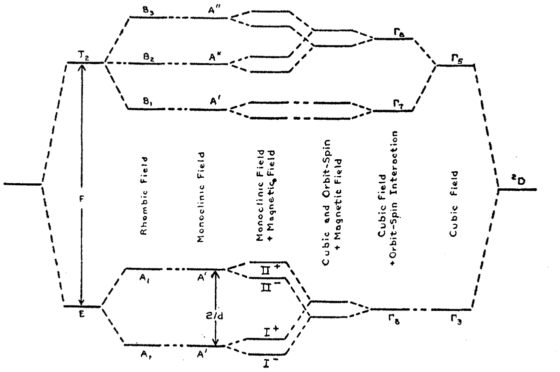

FIG. 1. The diagram shows how the energy levels arising from a ^2D configuration are influenced by the various fields. At either side of the diagram, the large separation produced by the cubic field is shown. At the left side, the rhombic field is superposed to give a resulting field of rhombic or monoclinic symmetry which removes the orbital degeneracy and yields five states. The inclusion of the spin produces no additional splitting until an external magnetic field is applied. Then all degeneracy is removed and the number of states is doubled. Proceeding now from the right side of the figure, the superposition of the orbit-spin forces on the cubic field removes only part of the degeneracy, and there are only six states even after the application of the magnetic field. The complete solution considers the combination of these two effects. Only the states branching from Γ_3 are normal states.

For the calculation of the magnetic susceptibility, we must know the energies of the lowest states (I and II in Fig. 1) and how these energies are affected by the magnetic field. The contribution of each state to the susceptibility is proportional to the population of that state, which, in turn, is proportional to the appropriate Boltzmann factor $\exp(-W_i/kT)$. Therefore the three upper states, having negligible population, will affect the susceptibility only as they modify the energies of the lower states.

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

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

[6] R. S. Mulliken, Phys. Rev. 43, 288 (1933).

[7] This relation is the analog of Eq. (1) of Schlapp and Penney's paper, reference 2.

THE MATRIX ELEMENTS

The matrix elements of the electric field may be determined for a one-electron system by direct quadrature using central wave functions. Since it is sufficient to consider only elements that are diagonal in L, the radial factor enters merely as a constant. Cu^{++} has a $d^9\,{}^2D$ configuration, and considerations similar to those underlying the Pauli reciprocity theorem tell us that it is equivalent to a one-electron system with the sign of the proportionality factors changed.[8] Most of the matrix elements which we need for the crystalline potential have been given by Schlapp and Penney.[9] However, we also need the elements of xy, *viz.:*

$$\left.\begin{aligned}&[xy](M_L\pm 2,\,M_L)=\pm\tfrac{1}{4}i\tau[(L\pm M_L+2)(L\pm M_L+1)(L\mp M_L)(L\mp M_L-1)],\\&[xy](M_L',\,M_L)=0,\qquad M_L'\neq M_L\pm 2,\qquad \tau=-2r^2/(2L+3)(2L-1).\end{aligned}\right\}\tag{3}$$

Then the nonvanishing matrix elements of the rhombic term (2) are:

$$\left.\begin{aligned}[Ax'^2+By'^2-(A+B)z'^2](M_L,\,M_L)&=[Ax^2+By^2-(A+B)z^2](M_L,\,M_L)\\&=\tfrac{1}{2}\tau(A+B)(3M_L^2-L^2-L),\\ [Ax'^2+By'^2-(A+B)z'^2](M_L\pm 2,\,M_L)&=[(A-B)(x^2\cos 2\alpha+xy\sin 2\alpha)](M_L\pm 2,\,M_L)\\&=-\tfrac{1}{4}\tau(A-B)[(L\pm M_L+2)(L\pm M_L+1)(L\mp M_L)(L\mp M_L-1)]^{\frac{1}{2}}\exp(\pm 2i\alpha).\end{aligned}\right\}\tag{4}$$

The matrix elements of $(\mathbf{L}\cdot\mathbf{S})$ are also given by Schlapp and Penney. We need only add the matrix elements of the Zeeman term. Introducing the definitions:

$$\mu\equiv\beta(\mathbf{L}+2\mathbf{S});\qquad \mathfrak{K}\equiv\beta\mathfrak{H}_z,\qquad \mathfrak{K}_x\equiv\beta\mathfrak{H}_x,\qquad \mathfrak{K}_y=\beta\mathfrak{H}_y,\tag{5}$$

one finds

$$\left.\begin{aligned}&\beta\mathfrak{H}\cdot(\mathbf{L}+2\mathbf{S})=\mathfrak{H}_x\mu_x+\mathfrak{H}_y\mu_y+\mathfrak{H}_z\mu_z,\\&[\beta\mathfrak{H}\cdot(\mathbf{L}+2\mathbf{S})](M_LM_S;\,M_LM_S)=\mathfrak{K}(M_L+2M_S),\\&[\beta\mathfrak{H}\cdot(\mathbf{L}+2\mathbf{S})](M_L\pm 1,\,M_S;\,M_LM_S)=\tfrac{1}{2}(\mathfrak{K}_x\mp i\mathfrak{K}_y)[L(L+1)-M_L(M_L\pm 1)]^{\frac{1}{2}},\\&[\beta\mathfrak{H}\cdot(\mathbf{L}+2\mathbf{S})](M_L,\,M_S\pm 1;\,M_LM_S)=(\mathfrak{K}_x\mp i\mathfrak{K}_y)[S(S+1)-M_S(M_S\pm 1)]^{\frac{1}{2}}.\end{aligned}\right\}\tag{6}$$

THE SECULAR MATRIX

The secular matrix $\mathbf{H}$, shown in Fig. 2, is diagonal in the elements of the cubic field. This results from the choice of the system of representation in which the Φ part of the orbital wave functions are proportional[10] to $\sin M_L\Phi$ and $\cos M_L\Phi$ rather than to $\exp(iM_L\Phi)$. It should perhaps be pointed out here that the matrix elements defined above are those appropriate to the exponential form of the wave function.[11] The following definitions have been introduced in

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[8] This change in sign accounts for the minus sign in our definitions of τ and q' in (3) and (7). For a general discussion of the sign of q' see reference 5.

[9] See reference 2, p. 672. Their a corresponds to our τ. In their first statement on p. 673, we may note the following minor correction: q and a should be replaced by q'/k_1 and a/c_1, respectively, where k_1 and c_1 are the constants computed for a one-electron system. For Cu^{++} the ratios are negative. The value of c_1 is the same as $-\tau$, while

$$k_1=[3\overline{r^4}/2(2L+5)(4L^2-9)(2L-1)];$$

cf. the last equation on p. 201 of Penney and Schlapp, Phys. Rev. **41** (1932).

[10] This is not a general statement but is true for the case $L=2$, as was demonstrated by Bethe.

[11] The secular matrix $\mathbf{H}$ is easily obtained from the matrix elements given above by first setting up the matrix $\mathbf{H}_x$ in the M_LM_S system of quantization. Then the unitary transformation $\mathbf{S}^{-1}\mathbf{H}_x\mathbf{S}$ gives the matrix $\mathbf{H}$ which is diagonal in the cubic field if $\mathbf{S}$ contains factors of the form

$$2^{-\frac{1}{2}}\begin{vmatrix}1&-1\\1&1\end{vmatrix}$$

for each pair of values $|M_L|$ and $-|M_L|$. We retain the spin matrices which are appropriate to the exponential form.

Λ^+					Λ^-				
Γ_3^+		Γ_5^+			Γ_5^-			Γ_3^-	
$2, \frac{1}{2}$	$0, \frac{1}{2}$	$-2, \frac{1}{2}$	$1, -\frac{1}{2}$	$-1, -\frac{1}{2}$	$1, \frac{1}{2}$	$-1, \frac{1}{2}$	$2, -\frac{1}{2}$	$0, -\frac{1}{2}$	$-2, -\frac{1}{2}$
$-6a+\mathfrak{R}$	η	$-A'-2\mathfrak{R}$	$A'/2$	$A'/2$	$-i\mathfrak{R}_y$	$\mathfrak{R}_x$	0	0	$\mathfrak{R}_x-i\mathfrak{R}_y$
η	$6a+\mathfrak{R}$	$-i\xi$	$3^{\frac{1}{2}}A'/2$	$-3^{\frac{1}{2}}A'/2$	$3^{\frac{1}{2}}i\mathfrak{R}_y$	$3^{\frac{1}{2}}\mathfrak{R}_x$	0	$\mathfrak{R}_x-i\mathfrak{R}_y$	0
$-A'-2\mathfrak{R}$	$i\xi$	$-F+\beta_3+\mathfrak{R}$	$A'/2$	$A'/2$	$-\mathfrak{R}_x$	$i\mathfrak{R}_y$	$-\mathfrak{R}_x+i\mathfrak{R}_y$	0	0
$A'/2$	$3^{\frac{1}{2}}A'/2$	$A'/2$	$-F+\beta_4-\mathfrak{R}$	$\frac{1}{2}A'-i\zeta-\mathfrak{R}$	0	$\mathfrak{R}_x+i\mathfrak{R}_y$	$i\mathfrak{R}_y$	$3^{\frac{1}{2}}\mathfrak{R}_x$	$\mathfrak{R}_x$
$A'/2$	$-3^{\frac{1}{2}}A'/2$	$A'/2$	$\frac{1}{2}A'+i\zeta-\mathfrak{R}$	$-F+\beta_5-\mathfrak{R}$	$-\mathfrak{R}_x-i\mathfrak{R}_y$	0	$-\mathfrak{R}_x$	$3^{\frac{1}{2}}i\mathfrak{R}_y$	$-i\mathfrak{R}_y$
$i\mathfrak{R}_y$	$-3^{\frac{1}{2}}i\mathfrak{R}_y$	$-\mathfrak{R}_x$	0	$-\mathfrak{R}_x+i\mathfrak{R}_y$	$-F+\beta_5+\mathfrak{R}$	$\frac{1}{2}A'-i\zeta+\mathfrak{R}$	$A'/2$	$-3^{\frac{1}{2}}A'/2$	$A'/2$
$\mathfrak{R}_x$	$3^{\frac{1}{2}}\mathfrak{R}_x$	$-i\mathfrak{R}_y$	$\mathfrak{R}_x-i\mathfrak{R}_y$	0	$\frac{1}{2}A'+i\zeta+\mathfrak{R}$	$-F+\beta_4+\mathfrak{R}$	$A'/2$	$3^{\frac{1}{2}}A'/2$	$A'/2$
0	0	$-\mathfrak{R}_x-i\mathfrak{R}_y$	$-i\mathfrak{R}_y$	$-\mathfrak{R}_x$	$A'/2$	$A'/2$	$-F+\beta_3-\mathfrak{R}$	$-i\xi$	$-A'+2\mathfrak{R}$
0	$\mathfrak{R}_x+i\mathfrak{R}_y$	0	$3^{\frac{1}{2}}\mathfrak{R}_x$	$-3^{\frac{1}{2}}i\mathfrak{R}_y$	$-3^{\frac{1}{2}}A'/2$	$3^{\frac{1}{2}}A'/2$	$i\xi$	$6a-\mathfrak{R}$	η
$\mathfrak{R}_x+i\mathfrak{R}_y$	0	0	$\mathfrak{R}_x$	$i\mathfrak{R}_y$	$A'/2$	$A'/2$	$-A'+2\mathfrak{R}$	η	$-6a-\mathfrak{R}$

FIG. 2. The **H** matrix. The terms in F are due to the cubic field, those in A' to the orbit-spin forces, and those in $\mathfrak{H}$ to the magnetic field. The other terms arise from the generalized rhombic term (2). The various symbols used are all defined in (6) and (7).

setting up the matrix in Fig. 2.

$$\begin{aligned} &a=-\tau(A+B)/2; && b=-\tau(A-B)/2;\\ &F=24q'D; && q'=-\overline{r^4}/126;\\ &\eta=2\cdot 3^{\frac{1}{2}}b\cos 2\alpha; && \xi=2\cdot 3^{\frac{1}{2}}b\sin 2\alpha;\\ &\zeta=3b\sin 2\alpha; && \beta_3=-6a;\\ &\beta_4=3a+3^{\frac{1}{2}}\eta/2; && \beta_5=3a-3^{\frac{1}{2}}\eta/2. \end{aligned} \tag{7}$$

In the matrix **H**, the terms in A' arise from the orbit-spin forces, those in $\mathfrak{R}$ from the magnetic field, and those in F from the cubic field. The other terms are due to the rhombic term in the crystalline field. Above the matrix we have indicated the relations between the matrix elements and the various group representations previously discussed. At the head of each column, are given the values of M_L and M_S appropriate to the exponential representation from which **H** was derived. These numbers serve to identify the matrix elements, but it must be remembered that, after the transformation to the trigonometric system of representation, M_L is no longer a good quantum number as regards sign.

When we proceed to the reduction of **H**, we note first that in the absence of the magnetic field the tenth degree matrix factors into two identical quintics. If a magnetic field is applied along the z-axis, the matrix still factors into two quintics (Λ^+ and Λ^-) which now differ in the sign of terms involving $\mathfrak{R}$. This simplifies matters greatly in the case $\alpha=0$, i.e., if the axes of the rhombic and cubic terms coincide, so that the resultant field has rhombic symmetry. Then it is possible to solve a quintic and obtain the principal susceptibility which corresponds to the application of the magnetic field along the z-axis. The other two principal susceptibilities are readily obtained from the first result by the cyclic permutation of the rhombic field parameters A, B and $-(A+B)$. In the general case that $\alpha\neq 0$, i.e., that the resultant field is monoclinic, this procedure fails, as the direction of the moment induced by the magnetic field directed along the coordinate axes may not agree with the direction of the applied field. That is, the magnetic axes (for which the direction of the induced moment is the same as that of the applied field) will not agree either with the axes of the cubic field or with those of the rhombic field but will lie in some intermediate position. When the magnetic field is applied in the xy plane, the secular matrix no longer factors. We then have to use a procedure somewhat similar to that developed by Kramers[12] in his most recent calculations on tysonite.

As we have already pointed out, we shall be satisfied to know the energy values of the states arising from only the configuration Γ_3. The effect on these states of the levels arising from Γ_5 may be computed by perturbation theory. However, since there are matrix elements between nearly degenerate states, the energy values cannot be obtained by the direct application of standard series perturbation technique. The procedure which we shall use and the derivation of the third order perturbation formulas for off-diagonal elements are given in the next section.

PERTURBATION TECHNIQUE

The $\mathbf{H}$ matrix is of the form $\mathbf{H}=\mathbf{H}_0+\lambda\mathbf{H}_1$, where $\mathbf{H}_0$ (the matrix of the cubic field) is diagonal and degenerate. The matrix $\mathbf{H}_1$, which contains the elements of the rhombic term, the orbit-spin interaction, and the magnetic field, has elements also on the main diagonal. In the zeroth approximation ($\lambda=0$), $\mathbf{H}$ factors into two parts γ_3 and γ_5 (Fig. 3) each of which has several equal roots. Referring to Fig. 1, we see that γ_3 should have four roots corresponding to the four levels arising from Γ_3, and Γ_5 should represent the six levels arising from Γ_5. We wish to know the roots of γ_3 to the order λ^3. Let m and n (with or without primes) refer to the elements of γ_3 and γ_5, respectively. We seek a unitary transformation matrix $\mathbf{S}=1+\lambda\mathbf{S}_1+\lambda^2\mathbf{S}_2$ such that $\mathbf{H}_2=\mathbf{S}^{-1}\mathbf{H}\mathbf{S}$ has no elements of the form $\mathbf{H}_2(m, n)$ to the order λ^2. This is a sufficiently good approximation unless we want the energy to the order λ^4. We require that $\mathbf{S}_1$ shall be of the form $\mathbf{S}_1(m, n)$ and that the elements of $\mathbf{S}_2$ be chosen to make $\mathbf{S}$ unitary. Then it is not difficult to show that[13]

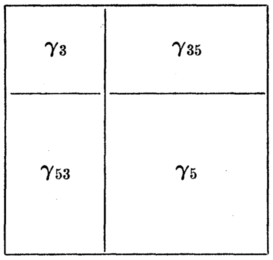

FIG. 3.

$$S_1(m, n)=-\frac{H_1(mn)}{H_0(mm)-H_0(nn)}=\frac{H_1(mn)}{h\nu(mn)},\qquad S_2(mm')=-\tfrac{1}{2}\sum_n\frac{H_1(mn)H_1(nm')}{h\nu(mn)h\nu(m'n)},\tag{8}$$

$$H_2(mm')=H_0(mm')\delta_m{}^{m'}+H_1(mm')+H_2''(mm')+H_2'''(mm'),\tag{9}$$

where

$$H_2''(mm')=\sum_n\frac{H_1(mn)H_1(nm')}{h\nu(m'n)}\tag{10}$$

and

$$H_2'''(mm')=-\tfrac{1}{2}\sum_{m'',\,n}\frac{H_1(mm'')H_1(m''n)H_1(nm')}{h\nu(mn)\cdot h\nu(m'n)}-\tfrac{1}{2}\sum_{n,\,m''}\frac{H_1(mn)H_1(nm'')H_1(m''m')}{h\nu(mn)\cdot h\nu(m''n)}+\sum_{n,n'}\frac{H_1(mn)H_1(nn')H_1(n'm')}{h\nu(mn)h\nu(m'n')}.\tag{11}$$

DETERMINATION OF THE ENERGY VALUES

By means of the perturbation formulas given above the tenth degree matrix is reduced to one of the fourth degree representing the states $\mathrm{I}^{\pm}$ and $\mathrm{II}^{\pm}$ of Fig. 1. The result, $\mathbf{H}_2$, is shown schematically in Fig. 4, where the terms which vanish with the magnetic field have been designated by the letter h.

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[12] H. A. Kramers, Proc. Amst. Acad. Sci. **35**, 1272 (1932).

[13] The matrix elements of S_2 are not uniquely defined until we impose an additional condition. It is convenient, but not necessary, to require that the S_2 be Hermitian; S_1 is never Hermitian.

$$\begin{array}{cccc} f(1,1)+h(1,1) & f(1,2)+h(1,2) & h(1,2^-) & h(1,1^-) \\ f(2,1)+h(2,1) & f(2,2)+h(2,2) & h(2,2^-) & h(2,1^-) \\ h(2^-,1) & h(2^-,2) & f(2,2)+h(2^-,2^-) & f(1,2)+h(2^-,1^-) \\ h(1^-,1) & h(1^-,2) & f(2,1)+h(1^-,2^-) & f(1,1)+h(1^-,1^-). \end{array}$$

FIG. 4. The $\mathbf{H}_2$ matrix.

We now apply a unitary transformation $\mathbf{S}_2^{-1}\mathbf{H}_2\mathbf{S}_2=\mathbf{H}_3$, such that $\mathbf{H}_3$ is diagonal in the absence of a magnetic field. The transformation $\mathbf{S}_2$ is easily found as, in the absence of a magnetic field, $\mathbf{H}_2$ factors into two identical quadratics. Let the resulting matrix elements be represented by $f'(i,j)\delta_j^i$ and $h'(i,j)$. Another transformation (essentially the application of Eq. (10)) eliminates all elements of the form $h'(1,2)$ and $h'(1,2^-)$ and gives us a new matrix $\mathbf{H}_4$ with elements only along the two main diagonals. The final energy values are obtained by the solution of two quadratics of the form:

$$\begin{vmatrix} f''(i,i)+h''(i,i)-W & h''(i,i^-) \\ h''(i^-,i) & f''(i,i)+h''(i^-,i^-)-W \end{vmatrix}=0. \qquad i=1,2. \tag{12}$$

The two roots of either determinant differ only in the sign of $\mathfrak{H}$. The energy values have such a form that they may conveniently be expressed as follows in terms of the direction cosines l, m and n, of the magnetic field:

$$W_1=-(1/d)\pm\mathfrak{H}\beta V_1+\mathfrak{H}^2\beta^2 w_1, \qquad W_2=+(1/d)\pm\mathfrak{H}\beta V_2+\mathfrak{H}^2\beta^2 w_2, \tag{13}$$

where

$$\left.\begin{aligned} V_i&=\{\boldsymbol{A}_i(l^2+m^2)+\boldsymbol{B}_i(l^2-m^2)+\boldsymbol{C}_i lm+\boldsymbol{E}_i n^2\}^{\frac{1}{2}}, \\ w_i&=\boldsymbol{A}_i^{(2)}(l^2+m^2)+\boldsymbol{B}_i^{(2)}(l^2-m^2)+\boldsymbol{C}_i^{(2)}lm+\boldsymbol{E}_i^{(2)}n^2. \end{aligned}\right\} \tag{14}$$

The coefficients which appear in V_1 and w_1 are defined by:

$$\left.\begin{aligned} \boldsymbol{A}_1&=1+2R(2-ud)+R^2\{2-3ud-2u^2d^2-\eta d^2\tan^2 2\alpha+\sigma(1+2u^2d^2)\}, \\ \boldsymbol{B}_1&=-3^{\frac{1}{2}}R\eta d\{2+R(3-2ud+2\sigma ud)\}, \\ \boldsymbol{C}_1&=-2\cdot 3^{\frac{1}{2}}R^2\xi d\{2ud-\sigma(3-4ud)\}, \\ \boldsymbol{E}_1&=1+4R(1+ud)+R^2\{-1+6ud+4u^2d^2+4\sigma\eta^2d^2(1-\tan^2 2\alpha)\}, \\ \boldsymbol{A}_1^{(2)}&=Rd\{\sigma(2-ud)+\tfrac{1}{2}R(1+2u^2d^2)(\sigma^2-1)-\tfrac{1}{2}R\eta^2d^2\tan^2 2\alpha\}, \\ \boldsymbol{B}_1^{(2)}&=-3^{\frac{1}{2}}R\eta d^2\{\sigma-Rud(1-\sigma^2)\}, \\ \boldsymbol{C}_1^{(2)}&=-3^{\frac{1}{2}}R^2\xi d^2\{2ud-\sigma^2(3-4ud)\}, \\ \boldsymbol{E}_1^{(2)}&=2Rd\{\sigma(1+ud)+R\sigma^2\eta^2d^2(1-\tan^2 2\alpha)-R\eta^2d^2\}, \end{aligned}\right\} \tag{15}$$

where $2/d$ is the final separation of the states I and II produced by the rhombic field; $2u$ is the difference between the diagonal elements of $\mathbf{H}_2$, i.e., $2u$ equals $f(1,1)-f(2,2)$, and is approximately equal to $12a$; F is the separation of Γ_3 and Γ_5 produced by the cubic field; $R=A'/F$, and $\sigma=1/dA'$. The coefficients which appear in V_2 and w_2 may be obtained from (15) by changing the sign of d (and consequently of σ) throughout.

CALCULATION OF THE PRINCIPAL SUSCEPTIBILITIES

The components of the magnetic moment vector may be calculated by the relation:

$$M_q=NkT(\partial/\partial\mathfrak{H}_q)\textstyle\sum_i e^{-W_i/kT}/\sum_i e^{-W_i/kT}. \qquad q=x,y,z. \tag{16}$$

Here we have supposed the energy expressed in terms of the x, y and z components of the magnetic field, whereas previously we have written the energy values in terms of the absolute value of the magnetic field and its direction cosines referred to the cubic field axes. This should cause no confusion, as we may replace the derivative $\partial/\partial\mathfrak{H}_q$ of (16) by its equivalent $(1/\mathfrak{H})(\partial/\partial s)$, where s has the values l, m, n, according as $q=x$, y, z, respectively. The magnetic axes, along which the principal susceptibilities are defined, are those for which the direction of the induced moment is the same as the direction of the applied field. With the notation $\theta=1/dkT$, the partition function for our problem is:

$$\sum_i e^{-W_i/kT}=2e^{\theta}\{1+(\mathfrak{H}^2\beta^2/2kT)[(V_1^2/kT)-2w_1]\}+2e^{-\theta}\{1+(\mathfrak{H}^2\beta^2/2kT)[(V_2^2/kT)-2w_2]\}. \tag{17}$$

In the denominator of (16) it is sufficient to consider only that portion of the energy which is independent of $\mathfrak{H}$, so that the sum (17) reduces to $2(e^{\theta}+e^{-\theta})$. For the numerator of (16) we may drop from the partition function the terms independent of $\mathfrak{H}$ and define a new quantity Z which is a homogeneous quadratic function of $\mathfrak{H}$, and may be written in the form:

$$Z\equiv(\mathfrak{H}\beta/kT)^2\{\mathbf{A}(l^2+m^2)+\mathbf{B}(l^2-m^2)+\mathbf{C}lm+\mathbf{E}n^2\}, \tag{18}$$

where

$$\mathbf{A}=\{\mathbf{A}_1-2kT\mathbf{A}_1^{(2)}\}e^{\theta}+\{\mathbf{A}_2-2kT\mathbf{A}_2^{(2)}\}e^{-\theta} \tag{19}$$

and similar expressions for $\mathbf{B}$, $\mathbf{C}$ and $\mathbf{E}$.

Let us choose a new set of coordinates, x'', y'', z, for which the direction cosines of the magnetic field are l'', m'' and n, and $\cos(x, x'')=\cos\phi$. If we require the term in $l''m''$ to vanish when Z is referred to the new axes, the angle ϕ will be defined by the relation $\tan 2\phi\equiv\mathbf{C}/2\mathbf{B}$ and then

$$Z'=(\mathfrak{H}\beta/kT)^2\{(\mathbf{A}+[\mathbf{B}^2+\mathbf{C}^2/4]^{\frac{1}{2}})l''^2+(\mathbf{A}-[\mathbf{B}^2+\mathbf{C}^2/4]^{\frac{1}{2}})m''^2+\mathbf{E}n^2\}. \tag{20}$$

The magnetic axes will coincide with the coordinate axes x'', y'', z, and, by (16), the principal susceptibilities will be given by the expression:[14]

$$\chi_i kT/N\beta^2\equiv M_i=\{k^2T^2/2\mathfrak{H}_i\beta^2(e^{\theta}+e^{-\theta})\}\partial Z'/\partial\mathfrak{H}_i. \qquad i=x'', y'', z. \tag{21}$$

By knowing the experimental values for the principal susceptibilities, it is possible to determine the parameters $1/d$, R, ud and α which appear in (20), and thus obtain some information about the magnitude and type of symmetry of the crystalline fields.

Temperature Rotation of the Magnetic Axes

Since the coefficients $\mathbf{C}$ and $\mathbf{B}$, whose ratio determines the direction of the principal magnetic moment, are functions of temperature, it follows that the direction of the principal moment in the crystal is also a function of temperature. The angle which the direction of maximum susceptibility makes with the axis of the cubic field is given by the relation $\tan 2\phi=\mathbf{C}/2\mathbf{B}$.

Experiments on magnetic susceptibility always furnish the resultant susceptibility, and the total paramagnetism of the metal ion is obtained by adding a correction equal to the diamagnetism of the anion and the water of hydration. In the case of the cupric hexahydrate sulphates, this diamagnetic correction is about ten percent of the total value at room temperature. For want of any information to the contrary, the diamagnetic correction is usually assumed to be the same for each of the three principal subsceptibilities, but there is no inherent reason why this must be true.

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[14] We find it convenient to discuss our results for the susceptibilities in terms of the quantity $M=\chi kT/N\beta^2$, which is 1/3 of the "effective magneton number." If Curie's law is obeyed M is a constant, and if the "spin-only" formula of Bose and Stoner is valid, the value of this constant is unity. The difference $M-1$ is a measure of the magnetic contribution of the orbit, and the variation of M with temperature measures the deviation from Curie's law.

Let us instead assume that one of the diamagnetic axes coincides with the z-axis of the crystalline fields, and that the other two diamagnetic axes lie in the xy plane with no particular correlation to the paramagnetic axes. Then we may introduce into the energy expression (13) a term

$$\mathfrak{H}^2\beta^2 G=\mathfrak{H}^2\beta^2[G_1(l^2+m^2+n^2)+G_2(l^2-m^2)+G_3lm], \tag{22}$$

which is the same for both states. G_1 is the mean diamagnetic correction and may be neglected if we use the experimental results which have been corrected in the usual way. The quantities G_2 and G_3 may be included in the sum (18) by redefining the coefficients:

$$\begin{aligned} \boldsymbol{B}&=\{\boldsymbol{B}_1-2kT(\boldsymbol{B}_1^{(2)}+G_2)\}e^{\theta}+\{\boldsymbol{B}_2-2kT(\boldsymbol{B}_2^{(2)}+G_2)\}e^{-\theta},\\ \boldsymbol{C}&=\{\boldsymbol{C}_1-2kT(\boldsymbol{C}_1^{(2)}+G_3)\}e^{\theta}+\{\boldsymbol{C}_2-2kT(\boldsymbol{C}_2^{(2)}+G_3)\}e^{-\theta}. \end{aligned} \tag{23}$$

The addition of these diamagnetic terms will modify both the formulas for the principal susceptibilities and the formula for the direction of the principal moment, for the resulting magnetic axes will be different from the axes of either the diamagnetic or paramagnetic parts alone. It is conceivable that reasonably small values of G_2 and G_3 may have an appreciable effect on the variation of the magnetic axes with temperature without greatly changing the values for the principal susceptibilities. If we write

$$G_2=6g_2Rbd/A' \quad \text{and} \quad G_3=-6g_3R^2bd/A', \tag{24}$$

the explicit formula for the direction of the magnetic axis is:

$$\tan 2\phi=\tfrac{1}{2}R\frac{\sin 2\alpha\{2ud(1-\tanh\theta/\theta)-3\sigma(1-kT/A')+4\sigma ud(1-kT/A')\tanh\theta\}-g_3kT/A'}{\cos 2\alpha(1-kT/A')\tanh\theta+g_2kT/A'}. \tag{25}$$

In general, then, there should be some variation of the direction of the magnetic axes with temperature. The direction of the magnetic axes will be constant in two particular cases: (1) when the axes of the rhombic and cubic terms coincide with the diamagnetic axes, i.e., when $g_3=\alpha=\xi=0$, the magnetic axes will coincide with the axes of the cubic field; (2) when the axes of the rhombic term make an angle of 45° with the cubic axes, and there is no diamagnetic asymmetry ($\eta=g_2=0$), the magnetic axes will make a constant angle of 45° with the axes of the cubic field.

It will be shown in the next section, that the above formula for the rotation of the magnetic axes with temperature is not entirely satisfactory. We have therefore repeated the calculations so as to ascertain the effect of a still more general rhombic term with components of higher degree in the crystalline potential. One finds that, after the addition of a fourth degree term of the form $\boldsymbol{D}x'^4+\boldsymbol{F}y'^4$, no further generality is secured by the addition of still higher order terms since the secular matrix then has as many independent arbitrary constants as is possible for a field of monoclinic symmetry. The calculations, therefore, were made by modifying the fourth degree terms, but the results are appropriate to the most general monoclinic field. The calculations are not included here because the results differ so slightly from those which we have described, but we will gladly furnish details to interested readers. It will suffice to point out the changes produced by the inclusion of the higher order rhombic terms. The **H** matrix would look like Fig. 2 except that the term $H(2, \frac{1}{2}; -2, \frac{1}{2})$ would be $(-A'-2\mathfrak{R}-i\rho)$ where ρ is a new constant, and the constants η, ξ, ζ, and the β_i would have slightly different definitions from those given in (7); in particular, ξ and ζ would now be independent of each other. The solution proceeds as before but results in the addition of higher order terms in the coefficients defined in (15). These higher order terms have only negligible effect on the principal susceptibilities, but one of these terms becomes important in Eq. (25) in the limiting case when $\eta=g_2=0$, as it may not vanish. Thus Φ may be a function of T, not constant, even in this limiting case. We conclude, however, that the rhombic term (2) is sufficiently general for all practical purposes.

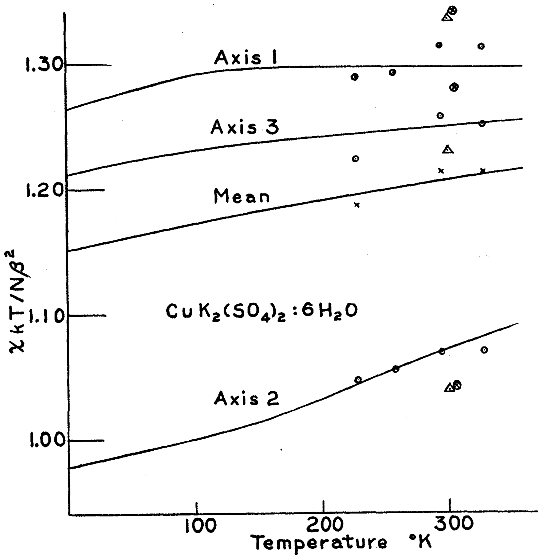

FIG. 5. Variation of the principal susceptibilities of $CuK_2(SO_4)_2 \cdot 6H_2O$ with temperature. Solid lines are computed curves. Experimental values: circles by Bartlett, triangles by Rabi, crossed circles by Krishnan and colleagues; crosses are means of Bartlett's values.

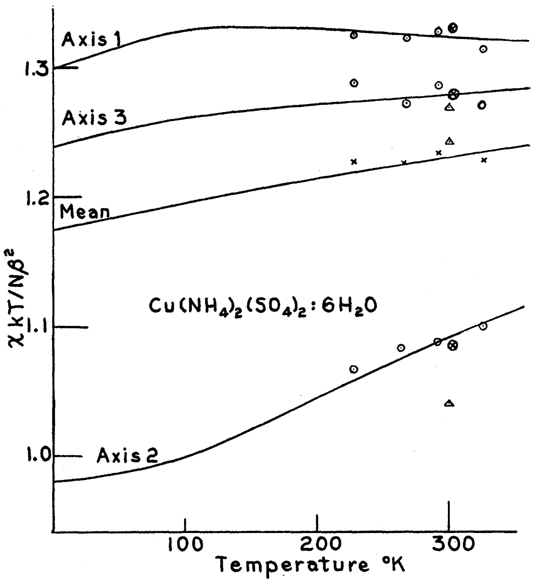

FIG. 6. Variation of the principal susceptibilities of $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$ with temperature. Solid lines are computed curves. Experimental values: circles by Bartlett, triangles by Rabi, crossed circles by Krishnan and colleagues; crosses are means of Bartlett's values.

COMPARISON WITH EXPERIMENT

Experimental data on the principal susceptibilities and the temperature rotation of the magnetic axes, have been obtained by Bartlett[15] for the two cupric hexahydrate sulphates: $Cu(NH_4)_2(SO_4)_2 : 6H_2O$ and $CuK_2(SO_4)_2 : 6H_2O$. The primary experimental results are the volume susceptibilities and these are probably accurate to about one percent. However, because the change in volume of the crystal with temperature was neglected, for lack of accurate data, and because of uncertainties in the diamagnetic correction, the final result for the molar susceptibilities of the metal ion may be in error by as much as two percent. The relative values are, of course, much better.

We have computed the variation of the principal susceptibilities with temperature, for these two substances, by adjusting the parameters to fit Bartlett's data. Figs. 5 and 6 show the computed curves and the experimental points of Bartlett. Note that we have plotted, as ordinate, the quantity $\chi kT/N\beta^2$ which should be independent of temperature if Curie's law is accurately obeyed. In each case we have included our curve for the mean susceptibility, averaged over the three axes, together with the means of Bartlett's points. The data of Rabi[16] and of Krishnan and his colleagues[17] for the principal susceptibilities at room temperature are also indicated, but we have disregarded these points entirely in choosing the parameters for our computed curves. The data for the potassium salt especially illustrate the diversity of the experimental results.

Agreement with Bartlett's data has been obtained for $CuK_2(SO_4)_2 : 6H_2O$ by assuming that the separations produced by the rhombic and cubic fields are respectively 360 and 21,300 wave numbers, that $\tan 2\alpha = -4$, and that $ud = 0.2$, which corresponds to choosing the coefficients of the rhombic term in the ratio: $A : B : C = 18 : -17 : -1$. For $Cu(NH_4)_2(SO_4)_2 : 6H_2O$, we find that the cubic and rhombic fields produce energy separations of 18,930 and 340 wave numbers, respectively, that $\tan 2\alpha = +3$, and that $ud = 0.25$, which corresponds to $A : B : C = 11 : -10 : -1$. In both cases the rhombic

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[15] B. W. Bartlett, Phys. Rev. **41**, 818 (1932); errata, Phys. Rev. **44**, 687 (1933).

[16] I. Rabi, Phys. Rev. **29**, 174 (1927).

[17] K. S. Krishnan, N. C. Chakravorty and S. Banerjee, Phil. Trans. **A232**, 99 (1933).

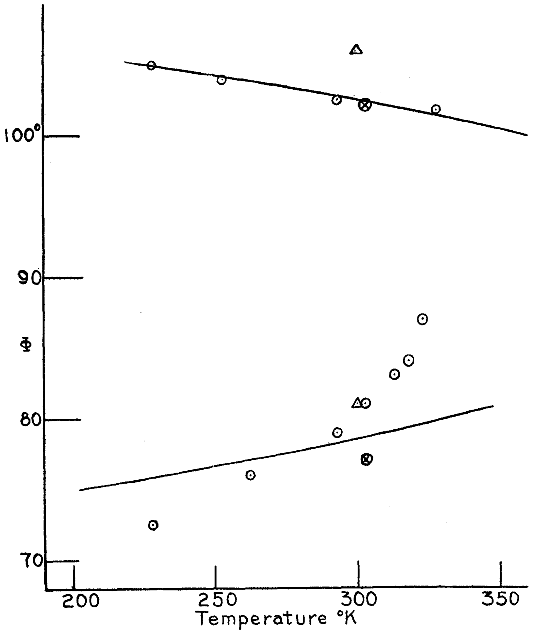

FIG. 7. Direction of the axis of maximum susceptibility as a function of temperature for crystals of $CuK_2(SO_4)_2\cdot$-$6H_2O$ (upper curve) and for $Cu(NH_4)_2(SO_2)_2\cdot 6H_2O$ (lower curve). The angles are referred to the crystallographic *c*-axis. Solid lines are computed curves. Experimental values: circles by Bartlett, triangles by Rabi, crossed circles by Krishnan and colleagues.

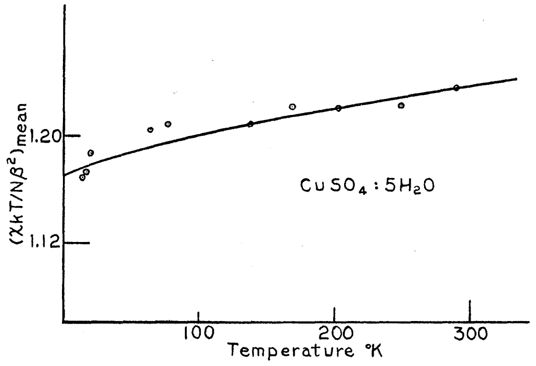

FIG. 8. Variation of the mean susceptibility of $CuSO_4\cdot$-$5H_2O$ with temperature. Experimental points by de Haas and Gorter.

term turns out to be approximately of the form $A(x'^2-y'^2)$.

Fig. 7 shows the agreement between the computed and observed values for the direction of the principal magnetic axes as a function of temperature. The experimental angles are referred to the crystallographic *c*-axis. Good agreement is obtained for the potassium salt by assuming: that the axis of the cubic field makes an angle of 110° 45′ with the crystallographic axis, that $g_2=0.15$, and that $g_3=-7.5$, with the other crystal field parameters given above. This corresponds to a diamagnetic asymmetry of about 40 percent of the mean diamagnetic correction. Even this large diamagnetic asymmetry does not give a rotation of the magnetic axes of the magnitude observed for the ammonium compound. Of course, it is possible to choose parameters which will give the desired rotation if we do not try to fit the susceptibility data at the same time. It seems quite evident that some additional factor must be introduced to account for the large rotation of magnetic axes with temperature.

Fig. 8 shows that the assumption of a crystalline field of predominantly cubic symmetry is also consistent with the mean susceptibility of $CuSO_4 : 5H_2O$. The experimental points are due to de Haas and Gorter[18] and the computed curve assumes that the rhombic and cubic fields produce energy separations of 212 and 18,500 wave numbers, respectively, with $\tan 2\alpha=4$ and $ud=0.3$.

CONCLUSION

The method outlined above is capable of giving good agreement with the experimental results on the variation of the principal susceptibilities with temperature. It also furnishes us some information about the type and magnitude of the electric field within the crystal. This information may be used to supplement the x-ray data to obtain more information about the actual crystal structure than can be obtained by x-ray analysis alone. This is particularly true in the case of crystals of low symmetry, where the x-ray data are difficult to interpret.

The two cupric hexahydrate sulphates which we have studied belong to the class called the Tutton salts. X-ray data on the cupric Tutton salts appear to be lacking, but the analysis of $Mg(NH_4)_2(SO_4)_2 : 6H_2O$ by Hofmann[19] shows that the six molecules of water are located at the vertices of a regular octahedron with the metal ion, Mg^{++}, at the center. Incidentally, this arrangement of the water molecules in the Tutton

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[18] W. J. de Haas and C. J. Gorter, Leiden Comm. 210d (1930).

[19] W. Hofmann, Z. Krist. **78**, 319 (1931).

salts is consistent with that deduced for $NiSnCl_6 : 6H_2O$ by Pauling[20] and for $NiSO_4 : 6H_2O$ by Beevers and Lipson.[21] The sulphate groups and the alkali or ammonium cations are situated at greater distances. It therefore seems logical to associate the predominant cubic field with the six water molecules, and to assume that the other groups produce the rhombic field which, when superposed on the cubic field, gives a resulting field of monoclinic symmetry. Our choice of parameters for the rhombic term, $A \backsimeq -B$ and $\alpha \backsimeq 45°$, suggests the location of the ionic groups, $SO_4^=$ and K^+ or NH_4^+, on two nearly orthogonal axes orientated at approximately 45° to the axes of the cubic field. However, the actual arrangement is probably not as simple as this.

It is a surprising fact that the mean susceptibility of $CuSO_4 : 5H_2O$ may be approximated over a wide range of temperature on the assumption that the crystalline field has predominantly cubic symmetry. Here the source of the cubic field is not obvious. However, one may suppose that some of the water molecules are shared in such a way as to give the octahedral arrangement around each metal ion. Of course, the agreement between the calculated and observed mean susceptibility may be only a coincidence, but the fact that the color of the blue vitriol is the same as that of the hexahydrates is another indication of similar group structures within the crystals. Furthermore, Gorter[22] has shown that, while D (the coefficient of the cubic term in (1)) is positive for an octahedral arrangement of six water dipoles, it would be negative for a tetrahedral or cubic arrangement of four or eight water dipoles, necessitating an inversion of Fig. 1. This would, presumably, alter the calculated dependence of the susceptibility on temperature and thus spoil the agreement with experiment. Data on the principal susceptibilities of this salt would be very welcome. Since the copper sulphate, pentahydrate, crystallizes in the triclinic form, the x-ray analysis is extremely difficult, and the magnetic analysis may point the way to a solution.

The important discovery by Bartlett,[15] that the direction of the principal magnetic axis is a function of temperature, is of considerable interest, and we have attempted to give an explanation for this result. We have shown that the changes of population of the various states with temperature does cause a rotation of the principal axis provided that the crystalline field has less than rhombic (e.g., monoclinic) symmetry. Unfortunately, the rotation of axes which we calculate using reasonable values of the crystal parameters is much too small in the case of the ammonium salt, and agreement is obtained in the case of the potassium salt only by assuming a large asymmetry in the diamagnetic correction. It is necessary to look for other or additional causes for the large rotation in the case of the ammonium salt. However, it may well be that the rotation of axes due to the repopulation of states is the important factor in other materials which have only feeble rotation.

A factor which has been entirely neglected is the thermal expansion of the crystal. Again experimental data are lacking, but it seems reasonable to expect asymmetrical thermal expansion in monoclinic crystals which are known to exhibit asymmetrical optical and magnetic properties. It is conceivable that, for certain critical arrangements, a slight asymmetric expansion might modify considerably the symmetry of the crystalline field, and thus cause the direction of the magnetic axes to change. For example (cf. Eq. (25)) suppose that α were very nearly 45°; then a slight asymmetrical expansion which would cause α to approach 45° would thereby produce a rapid rotation of the magnetic axes. The observed rotation (Fig. 8) for the ammonium salt suggests an approach to such a critical position. Even symmetrical thermal expansion will cause the crystal parameters to vary with temperature. We hope to have some data on the principal coefficients of thermal expansion of these cupric sulphates in the near future so that we may estimate the importance of this effect.

I wish to express my sincere thanks to Professor J. H. Van Vleck for his invaluable advice and constant encouragement during the course of this work. It is also a pleasure to acknowledge a grant from the Wisconsin Alumni Research Foundation which made the latter part of this work possible.

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[20] L. Pauling, Z. Krist. **72**, 482 (1930).

[21] C. A. Beevers and H. Lipson, Z. Krist. **83**, 123 (1932).

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