

The Principal Magnetic Susceptibilities of $\text{K}_3\text{Fe}(\text{CN})_6$

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that there are eight rather than six electrons to be housed in the five levels of Fig. 1. Hence regardless of whether Fig. 1 is upright or inverted, two electrons can have private orbitals without materially diminishing the energy, provided the rhombic splitting in Fig. 1 is small. To explain the observed diamagnetism of $K_2Ni(CN)_4$, one is thus led to predict a square (tetragonal) rather than tetrahedral configuration for the $Ni(CN)_4^{--}$ ion. This prediction is confirmed by x-ray measurements¹⁹ on $BaNi(CN)_4 \cdot 4H_2O$. On the other hand, $Ni(NH_3)_4SO_4$ is paramagnetic, and this fact suggests that there may be a tetrahedral structure for the group $(NH_3)_4$.

Our arguments to explain the diamagnetism of $K_4Fe(CN)_6$ apply equally well to diamagnetic cobaltic compounds such as the cobaltammines, since Co^{+++} is isoelectronic with Fe^{++} . The writer has shown elsewhere²⁰ that if the coordination number is six, and if (1) is valid (the sulphate rather than cyanide case), cobaltous compounds should show marked anisotropy and deviations from Curie's law, while the reverse should be true of nickel ones. If the coordination number is four, the roles of cobalt and nickel

should be interchanged. Blue and pink cobaltous salts are supposed to involve coordination numbers of four and six, respectively.²¹ It would therefore be interesting to see if one could prepare a blue cobaltous salt conforming closely to Curie's law. Attempts of R. B. Janes to do this have so far proved unsuccessful. The explanation may be either that the magnetic dilution is insufficient, so that the exchange forces between paramagnetic ions complicate the temperature dependence, or else that one is in the critical transition region wherein the mechanism for suppressing the magnetism below (1) just comes into play. In the latter event both states with $S=\frac{1}{2}$ and $S=3/2$ are populated, and the temperature variation will not be simple.

In conclusion, we may say that it should be regarded as reassuring and significant that all three mechanisms I, II, III permit a rational understanding of magnetism lower than that given by (1) and the Hund rule. Since none of the methods of approximation can be regarded as satisfactory from a quantitative standpoint, a property which is common to all three must be regarded as on a much firmer basis than if it is characteristic only of one approach.

The writer wishes to thank Mr. John Howard for interesting and valuable discussions.

¹⁹ H. Brasseur, A. de Rassenfoss and J. Piérard, *Zeits. f. Krist.* **88**, 210 (1934).

²⁰ J. H. Van Vleck, *Phys. Rev.* **41**, 208 (1932). In this connection see reference 10 regarding the relation between coordination number and the sign of the crystalline field.

²¹ R. Hill and O. R. Howell, *Phil. Mag.* **48**, 833 (1924).

The Principal Magnetic Susceptibilities of $K_3Fe(CN)_6$

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The magnitudes, anisotropy and temperature dependence of the principal magnetic susceptibilities of $K_3Fe(CN)_6$ are calculated by the method of crystalline potentials, and prove to be in good agreement with experiment. The assumption is made that the interatomic forces in the $Fe(CN)_6^{--}$ complex destroy Russell-Saunders coupling. This results in a susceptibility corresponding to *one* free electron spin with a contribution, except at very low temperatures, from the unquenched orbital angular momentum. The effect of the latter is sufficient to make the susceptibility at room temperature almost twice as large as the value which would be obtained if the spin alone were considered. The superposition of a small rhombic

crystalline field suffices to produce the large observed magnetic anisotropy. The behavior of the susceptibility of $K_3Fe(CN)_6$ is in sharp contrast to the higher effective magneton numbers and magnetic isotropy of many ferric compounds, such as the sulphates. In these the ground state of Fe^{+++} is the normal state of the free ion, namely a 6S state, so that five spins contribute to the susceptibility. Although the calculations ostensibly use the method of crystalline potentials, they are really based on general group properties and so apply even if the bonds in the cyanide are covalent, as they probably are, rather than ionic.

INTRODUCTION

THE magnetic measurements made by Jackson¹ on single crystals of $K_3Fe(CN)_6$ in the temperature range 75°–290°K reveal, in addition to the abnormally low susceptibility reported by other investigators, a remarkable anisotropy amounting to almost 100 percent at low temperatures. Compounds of ferric iron in general exhibit a high degree of magnetic isotropy and a mean susceptibility corresponding to a spin of 5/2. This latter behavior is to be expected if the Fe^{+++} ion in the crystal is in the 6S state, which is the ground state of the free ion.² In the second of the foregoing articles³ Van Vleck has demonstrated how the low susceptibility and magnetic anisotropy of $K_3Fe(CN)_6$ may be explained upon the assumption that the interatomic forces are sufficiently powerful to destroy Russell-Saunders coupling.⁴ A quantitative study of the susceptibility of this compound, based on this assumption, is presented in the present paper.

GENERAL PROCEDURE

The principal molar susceptibilities may be calculated from the expression⁵

$$\chi = \frac{L \sum_n [(W_n^{(1)}/kT) - 2W_n^{(2)}] e^{-W_n^0/kT}}{\sum_n e^{-W_n^0/kT}}. \quad (1)$$

Here L is Avogadro's number. The other constants are the coefficients of an expansion of the energy W_n in powers of the applied magnetic field \mathcal{H}

$$W_n = W_n^0 + W_n^{(1)}\mathcal{H} + W_n^{(2)}\mathcal{H}^2 + \dots \quad (2)$$

The summation is over all states of the system. In the so-called method of crystalline potentials⁶

this system is taken to be the magnetic ion subject to the constant ionic field of its neighbors in the crystal. The problem of finding the susceptibility is thus reduced simply to that of determining the relative energy levels W_n^0 of the magnetic ion in a crystalline field of a certain symmetry and finally the energies in the form (2) when a magnetic field is superposed. This is accomplished by means of a perturbation calculation in which the unperturbed system has the type of coupling most appropriate to the size of the crystalline field.

For the time being we shall use the language of the method of crystalline potentials and regard the interatomic forces of the $Fe(CN)_6^{---}$ complex as electrostatic. But we shall later see at the conclusion of the paper, that our calculations are independent of the nature of the bonding mechanism assumed.

In the present problem we assume that the coupling of the individual l 's to a resultant orbital angular momentum L is destroyed by a large cubic field, which is the dominant portion of the crystalline potential. In this respect our calculations differ from those of Schlapp and Penney,⁶ on Cr, Co and Ni compounds, wherein only the spin-orbit interaction is broken down. The unperturbed state of the Fe^{+++} ion in our problem is consequently taken to consist of five non-interacting $3d$ electrons. Under the action of the cubic potential the single d electron level splits into a triply and a doubly degenerate level, which we shall designate $d\epsilon$ and $d\gamma$ respectively.⁷ Gorter⁸ has shown that in an octahedral complex such as $Fe(CN)_6^{---}$ the triplet will lie lower. We now make the following approximation. We assume that the splitting of the d level is so large that we may neglect contributions to the susceptibility of perturbation matrix elements connecting the triplet and singlet levels. In order to uncouple the individual l 's, this splitting must, of course, exceed 3×10^4 cm⁻¹, the approximate separation⁹ of different multiplets arising from the d^5 configuration of Fe^{+++} .

¹ L. C. Jackson, Proc. Roy. Soc. A140, 695 (1933).

² See J. H. Van Vleck, Phys. Rev. 41, 208 (1932). For experimental data on the magnetic isotropy of ferric and manganous salts see Jackson, reference 1; Krishnan, Chakravorty and Banerjee, Phil. Trans. Roy. Soc. 232, 99 (1933); Krishnan and Banerjee, Nature 135, 873 (1935).

³ We shall refer to Van Vleck's first and second papers in this issue as V.V. I and V.V. II.

⁴ This explanation was first advanced by Van Vleck and W. G. Penney, Phil. Mag. 17, 961 (1934), footnote 6. See Linus Pauling, J. Am. Chem. Soc. 53, 1367 (1931); 54, 988 (1932) for an explanation of the low susceptibility based on the concept of localized orbitals.

⁵ See Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Ch. VII.

⁶ H. Bethe, Ann. d. Physik 3, 133 (1929); J. H. Van Vleck, reference 5, Ch. XI; W. G. Penney and R. Schlapp, Phys.

Rev. 41, 194 (1932); 42, 666 (1932); O. M. Jordahl, ibid. 45, 87 (1934).

⁷ For the full significance of the terms $d\epsilon$ and $d\gamma$ see Eqs. (5) and (6) of V.V. I.

⁸ C. J. Gorter, Phys. Rev. 42, 437 (1932).

⁹ Cf. footnote 12 in V.V. II.

Introducing the electron spin we obtain from the triply degenerate $d\epsilon$ level six single-electron states, among which the five electrons are to be distributed. The energy matrix for this $d\epsilon^5$ configuration is the same as that for a single electron in a $d\epsilon$ state except for a change in the signs of the proportionality factors in the perturbation. The reason for this is that five electrons represent a shortage of one from a complete and hence non-magnetic group of six electrons in the $d\epsilon^6$ configuration. Consequently, by virtue of our discarding the effect of the $d\gamma$ level, we may carry through the calculation of the energy levels as we would for a one-electron system except for this change in signs. The perturbation may then be written

$$H = [Ax^2 + By^2 - (A+B)z^2] + A'\mathbf{l} \cdot \mathbf{s} + \mathcal{H}\beta(m_l + 2m_s), \quad (3)$$

where A and B are the coefficients of the quadratic term of a rhombic crystalline potential, which is introduced in order to account for the observed magnetic anisotropy; A' is the coefficient of the spin-orbit coupling; \mathcal{H} is the applied magnetic field; and β is the value of the Bohr magneton $eh/4\pi mc$. The pattern of energy levels produced by the perturbation (3) for the $d\epsilon^5$ configuration is shown in Fig. 1.

Apparently we have specialized things somewhat in assuming that the rhombic potential is a quadratic function of x , y , z . But this is not really true, as the energy of our system in a rhombic field has three eigenvalues, of which one serves as a trivial additive constant since we are interested only in the relative energies. Hence the full generality of the secular problem arising from the lifting of the cubic degeneracy by a rhombic field is realized by (3), since (3) involves two independent constants, A and B , which determine the relative eigenvalues completely.

EXPRESSIONS FOR THE PRINCIPAL SUSCEPTIBILITIES

To calculate the energy values of the system one must diagonalize the secular matrix corresponding to the perturbation (3). The matrix elements are given by Schlapp and Penney and Jordahl.⁶ The matrix for the $d\epsilon^5$ configuration is

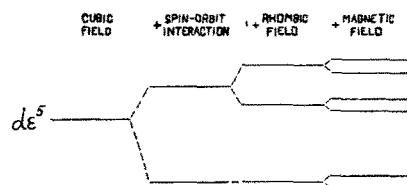


FIG. 1. Pattern of energy levels for the $d\epsilon^5$ configuration.

the same as the sextic corresponding to the irreducible representation Γ_5 given on p. 90 of Jordahl's paper.¹⁰ In the absence of a magnetic field this sextic factors into two identical cubics.

The similar behavior of two of the principal susceptibilities (see Fig. 2) suggests that the rhombic field, which is responsible for magnetic anisotropy, is very nearly axial in symmetry. For convenience the rhombic field in (3) may be written

$$(E+\Delta)x^2 + (E-\Delta)y^2 - 2Ez^2, \quad (4)$$

i.e., we set $A = E + \Delta$ and $B = E - \Delta$. We assume that Δ is small compared with E . In the limit when $\Delta = 0$ and the crystalline field has axial symmetry it is possible to solve rigorously the cubic secular equation involving the elements of the axial field and spin-orbit coupling. The complete matrix corresponding to (3) corrected by (4) is then diagonal in all but the elements containing Δ , the deviation from axial symmetry, and the magnetic field \mathcal{H} . A transformation is next made which leaves in off-diagonal positions only terms containing square or higher powers of Δ , which are negligible. Lastly, the effect of the magnetic field on the energy values is computed in the form (2). The final expressions for the relative energy levels are given below. The first set of three energy levels is for the magnetic field parallel to the a and b crystallographic axes.¹¹ The upper sign corresponds to the a axis,

¹⁰ Jordahl's matrix as a whole is inapplicable to our problem. His system is a d^9 configuration which is one electron short of a completed configuration d^{10} . Our system is a d^5 configuration and only because we have chosen to neglect the effect of the $d\gamma$ level, does it become one electron short of the closed configuration d^6 .

¹¹ Although $K_3Fe(CN)_6$ has monoclinic symmetry the deviation from orthorhombic symmetry is very slight ($\beta = 90^\circ 6'$). Consequently the crystallographic axes may be considered to coincide with the Cartesian axes along which the magnetic field is taken in the calculation. The susceptibilities which we calculate are for the magnetic field in the direction of these axes, whereas the experimental data with which the susceptibilities are compared are given for the magnetic field along the principal magnetic axes of the

the lower sign to the b axis. The second set of energy levels is for the field along the c axis.

$$\begin{aligned}
 W_{I^{a,b}} &= \frac{3m}{2} + \frac{u}{\lambda\xi} \left(-2n \pm \frac{4w\xi}{3} \right) K + \frac{1}{3\lambda} \left\{ -\frac{4u^2(u+v)^2}{\lambda^2\delta\xi} + \frac{4u^2}{m\xi} \pm \frac{(u+v)(\xi^{-1}+\xi)w}{3\lambda^2} \pm \frac{16u^2w}{3m\lambda\xi} \left[\frac{n\xi}{\xi} + \frac{u+v}{\delta\xi} \right] \right\} K^2, \\
 W_{II^{a,b}} &= \frac{3p}{2} + \frac{u}{\lambda\delta} \left(-2q \pm \frac{4w}{3\xi} \right) K + \frac{1}{3\lambda} \left\{ +\frac{4u^2(u+v)^2}{\lambda^2\delta\xi} + \frac{4u^2}{\rho\delta} \mp \frac{(u+v)(\xi^{-1}+\xi)w}{3\lambda^2} \pm \frac{16u^2w}{3p\lambda\delta} \left[\frac{q}{\delta\xi} + \frac{(u+v)\xi}{\xi} \right] \right\} K^2, \\
 W_{III^{a,b}} &= \mp \frac{4uw}{3\lambda} \left(\frac{\xi}{\xi} + \frac{1}{\delta\xi} \right) K - \frac{4u^2}{3\lambda} \left\{ \frac{1}{m\xi} + \frac{1}{p\delta} \pm \frac{4w}{3m\lambda\xi} \left[\frac{n\xi}{\xi} + \frac{u+v}{\delta\xi} \right] \pm \frac{4w}{3p\lambda\delta} \left[\frac{q}{\delta\xi} + \frac{(u+v)\xi}{\xi} \right] \right\} K^2, \\
 W_{I^c} &= \frac{3m}{2} - \frac{4u(\lambda-v)}{\lambda\xi} K - \frac{16u^2v^2}{3\lambda^3\delta\xi} K^2, \quad W_{II^c} = \frac{3p}{2} + \frac{4u(\lambda+v)}{\lambda\delta} K + \frac{16u^2v^2}{3\lambda^3\delta\xi} K^2, \quad W_{III^c} = 0.
 \end{aligned}$$

The meaning of the symbols is as follows:

$$\begin{aligned}
 K &= \mathcal{H}\beta; & \xi &= 3\lambda - 3v - u; \\
 u &= -2E\tau^2/7; & m &= u - v - \lambda; \\
 w &= -2\Delta\tau^2/7; & n &= u + v - \lambda; \\
 v &= -A'/2; & p &= u - v + \lambda; \\
 \lambda &= (u^2 + \frac{3}{2}uw + v^2)^{1/2}; & q &= u + v + \lambda; \\
 \delta &= 3\lambda + 3v + u; & \xi &= p/m.
 \end{aligned}$$

The coefficients A and B of the rhombic field are given by the expressions $u+w = -2A\tau^2/7$ and $u-w = -2B\tau^2/7$.

When these expressions are incorporated in (1) we obtain the principal magnetic susceptibilities. It is found convenient to express the susceptibilities in terms of the square of the empirical effective Bohr magneton number μ_B . This is defined by the relation $\chi_q = (L\beta^2/3kT)(\mu_B^2)_q$, where $q=a, b$ or c , corresponding to the crystallographic axis along which the magnetic field is directed.

COMPARISON WITH EXPERIMENT

The formulas for the principal susceptibilities involve three parameters, A' , A and B , which can be evaluated from the observed values of the three susceptibilities at a given temperature. Actually values of the parameters are chosen to reproduce as nearly as possible both the correct magnitudes and correct temperature dependence

crystal. Jackson's measurements show, however, that the latter system of axes, in the temperature range 75° to 290°K , is never out of coincidence with the crystallographic axes by more than a rotation by 3° about the b axis. For our purposes this small rotation may be ignored and the magnetic and crystallographic axes are taken to coincide.

of the susceptibilities (see Fig. 2). We thus obtain $A' = -510 \text{ cm}^{-1}$, $A\tau^2 = 108 \text{ cm}^{-1}$ and $B\tau^2 = 179 \text{ cm}^{-1}$. The value obtained for A' , the coefficient for spin-orbit coupling, is in excellent agreement with the value 500 cm^{-1} estimated by Van Vleck and Penney⁴ from spectral data. No appreciable difference would result if the value 500 cm^{-1} were used rather than 510 cm^{-1} . It is interesting that the spin-orbit coefficient can thus be indirectly calculated, say to within ten percent perhaps, by magnetic calculations.

In Fig. 2 it may be seen that the magnitude, anisotropy and temperature dependence of the magnetic susceptibilities are fairly well duplicated by the theoretical results. The slight divergence with increasing temperature which Jackson observed for the two similar susceptibilities along the a and b axes may well be due to

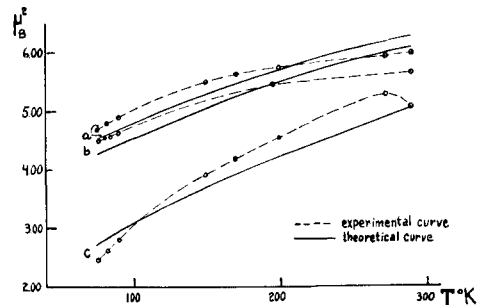


FIG. 2. Curves for the temperature variation of the square of the effective Bohr magneton number μ_B corresponding to the principal axes¹¹ a, b, c of $K_3\text{Fe}(\text{CN})_6$. By definition, μ_B is connected with the susceptibility χ through the relation $\mu_B^2 = (3kT/L\beta^2)\chi$.

variations in the force field in the crystal caused by the increasing energy of vibration. With a constant crystalline potential one would expect any magnetic anisotropy to diminish with temperature, if it changes at all, as the difference in the coefficients of the rhombic field becomes less important with respect to kT . The kink in the experimental curve for the susceptibility along the c axis probably also arises from a change in the crystalline field.

Some of the discrepancy with experiment may be due to the fact that we have neglected the matrix elements connecting $d\gamma$ and $d\epsilon$ which arise from the electrostatic energy $\sum e^2/r_{ij}$ coupling the five electrons together. Hence our calculations are not as accurate as those of Schlapp and Penney (except for their work on cobalt; cf. portion of V.V. II in fine print).¹²

GENERALITY OF OUR CALCULATIONS— CONCLUSION

We have so far used the language of the method of crystalline potentials for the sake of convenience in presenting the procedure of calculation. However, our calculations still apply with either the method of molecular orbitals or with the use of the Slater-Pauling localized bonds.

We have spoken of the Fe^{+++} ion subject to an ionic field whereas the ion is probably much less polar in $K_3Fe(CN)_6$. Consequently, an additional perturbation not explicitly included in (3) is the spilling over of some of the CN^- electrons onto the Fe^{+++} ion, which represents a tendency toward covalent bond formation. A convenient

way of treating covalent bonds is provided by the method of molecular orbitals, and is discussed more fully in V.V. II. In this method there are two types of $d\gamma$ levels, corresponding to the upper and lower roots of a secular equation which determines the proper linear combinations of the orbitals of the iron atom with the orbitals of the CN^- groups. (Cf., for instance, Fig. 2 in V.V. II.) The lower roots are bonding and, as they are each inhabited twice, do not contribute to the paramagnetic susceptibility. The upper roots are antibonding, and are so high that we consider them to be virtually uninhabited and neglect their effect. We are thus concerned only with the $d\epsilon$ orbitals. Fortunately they are nonbonding and do not combine with CN^- orbitals. Thus the covalent "spilling-over" effects do not vitiate our calculations of the magnetic susceptibility. This result is also true if we use Pauling's localized bonds instead of the method of molecular orbitals, for his $sp^3d\gamma^2$ directed bonds represent completed electron pairs which do not contribute to the susceptibility. Thus in his theory the magnetism results from the $d\epsilon^3$ orbitals, which are nonbonding and so amenable to our type of calculation.

Pauling assumed⁴ that the magnetism of the $d\epsilon$ group arises entirely from the spin. Our calculation has shown that actually the orbital angular momentum of the $d\epsilon$ group contributes appreciably to the susceptibility if the field is nearly cubic. This explains why the observed susceptibility is almost twice as high as that corresponding to one free spin.¹³

In conclusion I would like to thank Professor J. H. Van Vleck for suggesting this problem and for his invaluable advice during the course of the work.

¹² In Schlapp and Penney's article, reference 6, the inter-electronic energy $\sum e^2/r_{ij}$, which we shall call (a), is diagonalized in their unperturbed problem, but at the expense of considering the complete effect of (b) the cubic potential. They retained in Co only the part of (b) diagonal in L . We diagonalize (b) rather than (a) in the unperturbed system, since by hypothesis (b) is larger than (a) in the cyanides (unlike the sulphates). (Even at that we retain only matrix elements of (b) internal to the configuration d^6 . Otherwise, the problem involves an infinite number of states and is of hopeless complexity.) Fortunately, except in Co, there are no matrix elements of (b) nondiagonal in L in the states of high spin in which Schlapp and Penney were interested (cf. fine print in V.V. II.); otherwise their accuracy would be no higher than ours.

¹³ The spin-only value of μ_B is 1.73 for one free spin. The reason that Pauling did not seem to need orbital contributions to the susceptibility is that he apparently used the value $\mu_B = 2.00$ quoted by Bose, *Zeits. f. Physik* **65**, 677 (1930). This value is out of line with the higher values 2.3–2.4 reported by Jackson¹ and by Ishiwara, *Sci. Rep. Tohoku Univ.* **3**, 303 (1914); W. Biltz, *Zeits. f. anorg. Chemie* **170**, 161 (1928); and L. A. Welo, *Phil. Mag.* **6**, 481 (1928).