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Valence Strength and the Magnetism of Complex Salts

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Certain complex salts, notably ferro- and ferricyanides, have susceptibilities much lower than those predicted by the Bose-Stoner "spin only" formula. The first interpretation was that given by Pauling on the basis of (I) directed wave functions. In the present paper it is shown that alternative explanations are possible with (II) the crystalline potential model of Schlapp and Penney, or with (III) Mulliken's method of molecular orbitals. In any of the theories, the interatomic forces, if sufficiently large, will disrupt the Russell-Saunders coupling, and make the deepest state have a smaller spin, and hence smaller susceptibility, than that given by the Hund rule. This

situation is not to be confused with that in normal paramagnetic salts, such as sulphates or fluorides, where only the spin-orbit coupling is destroyed. The similarity of the predictions with all three theories is comforting, since any one method in valence usually involves rather questionable approximations. Because of this similarity, a preference between the theories cannot be established merely from ability to interpret the anomalously low magnetism of the cyanides. Covalent bonds, as in cyanides, seem to be more effective in suppressing magnetism than are ionic ones, as in fluorides, but so far the evidence to this effect is empirical rather than theoretical.

IN most salts of the iron group, the susceptibility has approximately the value

$$\chi = 4N\beta^2 S(S+1)/3kT, \quad (1)$$

where β is the Bohr magneton $he/4\pi mc$, and where the spin S has the value given by the Hund rule that the ground state is that of maximum multiplicity compatible with the Pauli principle. Formula (1) was suggested by Bose and Stoner. The theoretical explanation has been known for some time,¹ and is that the crystalline field is so strong as to destroy the coupling of the spin angular momentum S and orbital angular momentum L to a quantized resultant J . It can be shown that with such an "electric Paschen-Back effect," the orbital magnetism is largely quenched, and the susceptibility has nearly the value (1).

There are, however, certain compounds of elements of the iron group, notably iron cyanides and the various cobaltammines, for which the susceptibility has a value very much lower than that given by (1). In fact, these compounds are diamagnetic if they involve a complex ion containing an even number of electrons (e.g., $\text{Fe}(\text{CN})_6^{4-}$), or have a susceptibility of an order of magnitude corresponding to one free spin, i.e., to $S = \frac{1}{2}$ in (1), if this number is odd (e.g., $\text{Fe}(\text{CN})_6^{3-}$). The first specific model accounting for this behavior was given by Pauling,² but the

explanation may be couched in more general language as follows: the interatomic forces are so very large as to destroy not merely the spin-orbit but also the Russell-Saunders coupling, and make the deepest state that of lowest possible spin rather than of maximum spin as given by the Hund rule.³ Large spin would be an advantage as far as a free atom is concerned, but the point which we wish to make is that the interatomic energy is decreased by lowering the total spin regardless of whether one makes the calculation in any of three ways:

(I) the directed electron pair bond, sometimes called the Heitler-London-Pauling-Slater approximation,

(II) the method of crystalline fields, particularly adapted to ideally ionic compounds, and

(III) Mulliken's method of molecular orbitals.⁴

There is thus a formal similarity between the results of various approaches, in many respects paralleling that on the subject of directional valence stressed in the preceding paper. The cyanide anomalies have been previously interpreted only on the basis of I, although Mulliken⁴ did state that magnetic behavior might often be equally intelligible with the mechanism III.

The particular examples which we shall consider are compounds in which the central or

¹ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Chap. XI.

² L. Pauling, *J. Am. Chem. Soc.* **53**, 1367 (1931); L. Pauling and M. L. Huggins, *Zeits. f. Krist.* **87**, 205 (1934).

³ For this rule see, for instance, Pauling and Goudsmit, *The Structure of Line Spectra*, p. 165.

⁴ R. S. Mulliken, *Phys. Rev.* **40**, 55 (1932).

paramagnetic atom has a coordination number of six resulting from six neighboring atoms or ions octahedrally arranged. The clusters $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_6^{3-}$, FeF_6^{3-} , in $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{K}_3\text{Fe}(\text{CN})_6$, $(\text{NH}_4)_3\text{FeF}_6$, respectively, are structures of this character. It is not necessary that the crystal as a whole have cubic symmetry. For instance, $\text{K}_3\text{Fe}(\text{CN})_6$ is monoclinic. From these examples we trust it will be sufficiently clear how the similarity between the various methods is demonstrated in other cases.

The deepest state of the Fe^{++} ion is a 6S term, and indeed the observed susceptibility⁵ of $(\text{NH}_4)_3\text{FeF}_6$ approximately equals that given by (1) with $S=5/2$. The susceptibility⁶ of $\text{K}_3\text{Fe}(\text{CN})_6$, however, is much nearer the value given by (1) with $S=\frac{1}{2}$. The interatomic forces should thus be relatively more important in the cyanides than in the fluorides, and it is, in fact, known that the former are firmer compounds than the latter.

I. THE METHOD OF DIRECTED ELECTRON PAIR BONDS

The magnetic behavior of $\text{Fe}(\text{CN})_6^{3-}$ is explained by Pauling on the basis of the structure $\text{Fe}^{3+}(\text{CN})_6$. This model need not be literally true, but is taken to be sufficiently typical, i.e., a sufficiently common phase in the resonance through various stages of polarity, to serve for purposes of discussion. According to Pauling,² the Fe^{3+} ion attaches its six atoms of coordination by means of six $sp^3d\gamma^2$ electron pair bonds. These six bonds consume the $4s$, $4p$, and $d\gamma$ states,⁷ and house six electrons of Fe^{3+} . (Only one electron can be assigned to a state of the central atom which is used for bonding purposes; for if a state houses two electrons, their spins compensate each other, and they are not free to form electron pair bonds with outside atoms.) The Fe^{3+} ion has 11 electrons in all to house (apart from completed inner shells). The five electrons not absorbed by the electron pair bonds can only be accommodated in the three $3d\epsilon$ states. Thus two of these states will be filled

twice. The electrons which are thus "doubled up" must have their spins antiparallel because of the Pauli principle, and hence make no contribution to the susceptibility. The fifth electron, however, has a free spin, so that the susceptibility should be given approximately by (1) with $S=\frac{1}{2}$ provided one can overlook orbital contributions to the susceptibility. Actually they are not negligible, as Howard shows in the next paper. In $\text{Fe}(\text{CN})_6^{4-}$, there is an additional electron to house, so that the fifth electron loses its private state, and there can only be diamagnetism, in agreement with experiment.

II. THE METHOD OF THE CRYSTALLINE POTENTIAL

The simplest model for explaining the varying magnetic properties is that used with success by Penney and Schlapp⁸ primarily on hydrated sulphates of the rare earth and iron groups. The basic assumption is that the effect of neighboring atoms can be represented by means of a static potential. One may distinguish between three cases depending on the strength of the crystalline field: (a) the field is so weak that the inner quantum number J has a meaning (b) it is so large as to prevent J , but not L or S from being a good quantum number, and (c) it is still more powerful, and able to destroy Russell-Saunders coupling, i.e., the compounding of the individual l 's to a resultant L , so that L loses its validity as a quantum number. Cases (a) and (b) are those studied by Penney and Schlapp, (a) being characteristic of the rare earths, and (b) of the hydrated sulphates of the iron group. We shall now show that (c) furnishes an explanation of the behavior of the cyanides and other salts having abnormally low susceptibilities.

In the compounds in which we are at present interested, the crystalline field is of dominantly cubic symmetry. In a field of this symmetry type, it can be shown by means of group theory,⁹ or otherwise, that a d electron has the Stark pattern shown in Fig. 1. The separation of the

⁵ E. Cotton-Feytis, *Ann. Chim.* **4**, 9 (1925).

⁶ Cf. for instance, L. C. Jackson, *Proc. Roy. Soc.* **A140**, 695 (1933).

⁷ For explanation of the notation $d\gamma$, $d\epsilon$ see Eqs. (5)–(6) of the preceding paper in this issue.

⁸ W. G. Penney and R. Schlapp, *Phys. Rev.* **41**, 194 (1932); R. Schlapp and W. G. Penney, *ibid.* **42**, 666 (1932); O. Jordahl, *ibid.* **45**, 87 (1934); R. Janes, *ibid.* **48**, 78 (1935).

⁹ See, for instance, H. Bethe, *Ann. d. Physik* **3**, 143 (1929).

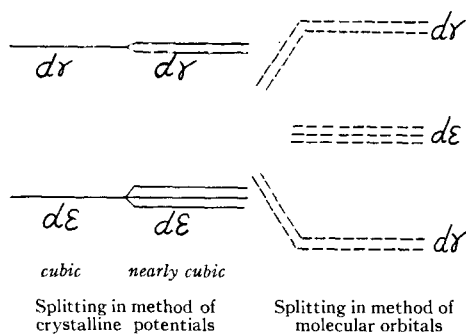


FIG. 1.

FIG. 2.

levels which branch out from a common origin on the left is, by hypothesis, comparatively small, and owes its existence to the deviations of the field from perfect cubic symmetry. Do not confuse Fig. 1, which is for one electron, and the closely related crystalline Stark diagrams given by Penney, Schlapp, and Van Vleck for whole atoms in which the electrons are space quantized collectively rather than individually. Fig. 1 is right side up, as Gorter¹⁰ shows, so long as the negative ions surrounding the paramagnetic cation are octahedrally arranged. Fig. 1 should be inverted in case the coordination number is four rather than six, i.e., the symmetry tetrahedral rather than octahedral. Now if we assume the conventional polar structure $\text{Fe}^{+++}(\text{CN}^-)_6$, the Fe^{+++} ion has five electrons outside closed shells, and there are five electrons to be housed in the various states of Fig. 1. Clearly the deepest energy is obtained by assigning the five electrons to the three components of $d\epsilon$. Then all the electrons but one double up, and there is only one free spin, while in $\text{Fe}^{++}(\text{CN}^-)_6$ there would be no free spin. Thus with a sufficiently large field to make individual space quantization a good approximation, the deepest state is quite different from that 6S given by the Hund rule.

It is interesting to note the significance of the state $d^5 ^6S$ in terms of Fig. 1. Usually Russell-Saunders coupling involves collective quantization in such a way as not to permit any simple interpretation in terms of a one-electron diagram

such as Fig. 1. However, when the spin quantum number equals half the number of electrons, as in $d^5 ^6S$, the spins are all mutually parallel. Such an alignment is possible only if each electron has its own private orbital. Hence a state of the configuration d^5 with $S=5/2$ involves one electron in each of the five levels of Fig. 1. This distribution has an invariant significance (one to a state) regardless of how the axis of space quantization is chosen. Hence this state must be an S state, as is also proved by other means and as is reflected in the high magnetic isotropy of manganous and ferric salts of the sulphate variety. When, however, one has the cyanide case, there are three different ways in which the five electrons may be distributed among $d\epsilon$, since the private orbital may be the lower, middle, or upper component of $d\epsilon$. True cubic symmetry is achieved only if the three components are populated equally. Hence $\text{K}_3\text{Fe}(\text{CN})_6$ can exhibit a high degree of magnetic anisotropy. This point is studied quantitatively by J. Howard in the next paper.

As we have seen, the energy due to the crystalline field is lowest when the Hund rule is broken down. However, the internal energy of the Fe^{+++} ion is lower with $S=5/2$ than with $S=\frac{1}{2}$. (This is the meaning of the Hund rule.) Thus whether the total internal plus external energy is lower or higher for $S=5/2$ than for $S=\frac{1}{2}$ is a question purely of the size of the crystalline potential relative to the strength of the Russell-Saunders coupling. The fact that both cases are actually realized suggests that the two energies are of the same order of magnitude, and such indeed appears to be the case. The crystalline fields deduced by Schlapp, Penney, Jordahl, and Janes⁸ for the hydrated sulphates usually amount to about 3 volts.¹¹

¹¹ In Cr^{+++} an over-all splitting of about 8 volts is obtained by Schlapp and Penney, a value which seems unduly high and out of line with their other results. As they intimate, the explanation of this discrepancy is probably that in Cr^{+++} , the computation of the splitting is unusually sensitive to small experimental errors in the determination of the absolute value of the susceptibility because the latter has very nearly the "spin-only" value in this particular ion. Schlapp and Penney employed the Leiden data on chrome alum. It is interesting to note that a splitting (3 volts) of about the usual size is yielded by Janes⁸ recent measurements on $\text{K}_2\text{Cr}(\text{SCN})_4\cdot 4\text{H}_2\text{O}$. Incidentally, the separation $17,200\text{ cm}^{-1}$ which Janes obtains in cupric salts relates to the over-all splitting, rather than the constant D as stated in his article, and so is not unreasonable.

¹⁰ C. J. Gorter, Phys. Rev. **42**, 437 (1932).

The strength of the Russell-Saunders coupling is measured by the separation of the various levels arising from the configuration d^5 in the free ion. Spectroscopic data indicate that this separation amounts to only about 4 or 5 volts.¹² Hence the crystalline field would not have to be much larger than in the examples studied by Schlapp and Penney in order to overpower the Russell-Saunders coupling,¹³ and so it is plausible that this situation is realized in the cyanides.

Even in the case studied by Schlapp and Penney, labeled (b) above, the separation between the various states of the configuration $3d^x$ is not larger than the crystalline potential. Consequently one naturally wonders whether they were justified in neglecting matrix elements between states of different L but similar S belonging to the same configuration. Neglect of matrix elements between states differing both in L and S is legitimate if the intervals between such states are large compared with the spin-orbit interaction, i.e., with multiplet widths. This condition is practically always fulfilled. In Fe^{+++} or Mn^{++} there can be no question of rigor, since the configuration d^5 has only one sextet state. Also in Cr^{++} or Fe^{++} (d^4 or d^6) there is only one quintet, while in Cu^{++} (d^9) there is only one state of any character, a doublet. In Cr^{+++} or Co^{++} , however, the states of highest multiplicity are 4F and 4P , while in Ni^{++} , they are 3F and 3P . The separation between these two states is only about 2 volts¹⁴ in either Co^{++} or

Ni^{++} . Spedding¹⁵ criticizes the work of Schlapp and Penney on the ground that they do not consider the perturbing effect of 3P in their calculations of the 3F state of Ni^{++} , or of 4P on the 4F of Cr^{+++} , Co^{++} . However, Spedding has overlooked the fact that in Cr^{+++} or Ni^{++} the Stark component of the F level which is important for the magnetic calculations is that which belongs to the representation A_2 ¹⁶ of the cubic group. On the other hand, 3P or 4P belongs to the representation T_1 , and so is incapable of perturbing A_2 , if the field is really cubic. This statement is not quite true when one allows for the fact that the spin-orbit distortion makes the symmetry different from that characteristic of orbit alone. In other words, one ought rigorously to consider the irreducible transformation properties of the spin-orbit rather than just orbital wave functions. However, the spin-orbit distortion is subordinate, and so the perturbation due to this cause is negligible. Furthermore the Stark component A_2 of 3F or 4F involves different rhombic representations than do 3P or 4P , and so cannot be perturbed by the latter even when one considers the deviations from cubic symmetry, as long as rhombic symmetry is preserved. Hence Schlapp and Penney's conclusions on the nearly perfect magnetic isotropy of Ni^{++} , Cr^{++} and their close conformity to (1), are unaffected. In the case of Co^{++} , the ground level is the Stark component T_1 of $d^7\ ^4F$, and can be perturbed by $d^7\ ^4P$. We hope to study this effect later more fully. In Co^{++} , anyway, the agreement which Schlapp and Penney obtained with experiment was qualitative rather than quantitative. Rough preliminary examination suggests that it will probably be improved by considering the perturbation by 4P . Hence, we conclude that all the vital features of Schlapp and Penney's calculations are unaffected by considering the incipient breakdown of Russell-Saunders coupling, and that in Co^{++} the quantitative agreement may actually be bettered.

III. THE METHOD OF MOLECULAR ORBITALS

This method differs from the crystalline field procedure II in that the structural unit for the wave function is the whole complex ion (e.g., $\text{Fe}(\text{CN})_6^{3-}$) rather than the single central atom. Both II and III utilize one-electron wave functions, and so group theory based on symmetry properties can still be used to obtain information about the character of the levels. However, there is the difference that if a central orbital is bonding, a given representation appears more often than in method II because of the fact that, in the language of the preceding paper, there are both central and attached orbitals belonging to the same irreducible representation. The proper

¹² Spectroscopic data are not available on the Fe^{+++} ion. However, the separation of the various terms belonging to the configuration d^5 in Fe^{+++} should be somewhat greater than (probably a little less than double) the corresponding separations in the homologous ion Cr^+ , and the interval $d^5\ ^6S-d^5\ ^4G$, for instance, is known to be 2.5 volts in Cr^+ .

¹³ Unfortunately it does not appear possible to estimate directly from theoretical considerations the crystalline splitting to be expected even with an ideal ionic structure and assumed interatomic separations obtained from Pauling's atomic radii. So one can only deduce the splittings empirically from the magnetic data. The difficulty is that one does not know well enough the effective charge Z to be used in computing the d wave functions. Clearly Z should be somewhat greater than 4, the value corresponding to perfect screening, and somewhat less than the effective charge Z_{ip} deduced from ionization potentials, as the value of Z to be used in computing \bar{r}^2 etc. is less than that involved in $1/\bar{r}$. Extrapolated spectroscopic data indicate that Z_{ip} is about 6. In unpublished calculations, Howard finds that the interval $d\gamma-d\epsilon$ amounts to 4 volts if $Z=4$ and to 1 volt if $Z=6$, provided the further assumptions are made that the distance $\text{Fe}-\text{F}$ is 1.91 Å, and that the F^- ions act like point charges.

¹⁴ The intervals $d^7\ ^4F-d^7\ ^4P$ of Co^{++} and $d^8\ ^3F-d^8\ ^3P$ of Ni^{++} have not been observed directly, but probably do not differ greatly from the intervals $d^7(^4F)4s^2-d^7(^4P)4s^2$ of Co I, and $d^8(^3F)4s^2-d^8(^3P)4s^2$ of Ni I, respectively. These latter intervals are known and are both 1.9 volts. That the addition of the $4s$ electrons does not change too materially the separations of the core states is indicated, for instance, by the fact that the frequency difference $d^4(^3F)4s\ ^4F-d^4(^3G)4s\ ^4G$ in Cr II deviates only 4 percent from the difference $d^4\ ^3F-d^4\ ^3G$ in Cr III (see Bacher and Goudsmit's tables).

¹⁵ F. H. Spedding and G. C. Nutting, J. Chem. Phys. 2, 421 (1935).

¹⁶ For explanation of the notation for the group representations see R. S. Mulliken, Phys. Rev. 43, 279 (1933).

linear combination of such central and attached orbitals is found by solving a secular equation. In the case of the octahedral group, the wave functions belonging to the irreducible representation E_g are

$$\psi(E_g) = \alpha\psi(3d\gamma_1) + (1-\alpha^2)^{1/2}(1/12)^{1/2}(2\psi_3 + 2\psi_6 - \psi_1 - \psi_4 - \psi_2 - \psi_5), \quad (2a)$$

$$\psi''(E_g) = (1-\alpha^2)^{1/2}\psi(3d\gamma_1) - \alpha(1/12)^{1/2}(2\psi_3 + 2\psi_6 - \psi_1 - \psi_4 - \psi_2 - \psi_5), \quad (2b)$$

$$\psi'(E_g) = \alpha\psi(3d\gamma_2) + (1-\alpha^2)^{1/2}(\psi_1 + \psi_4 - \psi_2 - \psi_5), \quad (3a)$$

$$\psi'''(E_g) = (1-\alpha^2)^{1/2}\psi(3d\gamma_2) - \alpha^{1/2}(\psi_1 + \psi_4 - \psi_2 - \psi_5), \quad (3b)$$

where the wave function of attached atom i is denoted by ψ_i , and the explicit forms of the central wave functions $\psi(d\gamma)$ are as given in Eqs. (5)–(6) of the preceding paper. Attached atoms 1, 4 are supposed located on the x axis; 2, 5 on the y ; and 3, 6 on the z . The value of α is determined, at least in principle by solving a secular equation. Similarly, the wave functions corresponding to A_{1g} and T_{1u} are

$$\psi(A_{1g}) = \beta\psi(4s) + (1-\beta^2)^{1/2}(\frac{1}{6})^{1/2}(\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6), \quad (4a)$$

$$\psi(T_{1u}) = \gamma\psi(4p\sigma_x) + (1-\gamma^2)^{1/2}(\frac{1}{2})^{1/2}(\psi_1 - \psi_4), \quad (5a)$$

$$\psi'(T_{1u}) = \gamma\psi(4p\sigma_y) + (1-\gamma^2)^{1/2}(\frac{1}{2})^{1/2}(\psi_2 - \psi_5), \quad (6a)$$

$$\psi''(T_{1u}) = \gamma\psi(4p\sigma_z) + (1-\gamma^2)^{1/2}(\frac{1}{2})^{1/2}(\psi_3 - \psi_6), \quad (7a)$$

together with four other wave functions (4b)–(7b) which are similar except that β , $(1-\beta^2)^{1/2}$ are replaced, respectively, by $(1-\beta^2)^{1/2}$, $-\beta$, etc. The notation $p\sigma_x$ means a p state with $m_l=0$ when the quantization is relative to the x axis. The basic theoretical principles underlying the construction of wave functions such as (2)–(7) are outlined in the preceding article.¹⁷

The lower roots of the quadratic secular equations associated with (2)–(7) represent lower energy than for the free atom, i.e., are bonding levels, while the upper roots give higher energy than for the free atoms, i.e., are antibonding.

The $d\epsilon$ wave functions are nonbonding, as shown in the previous paper. The situation is illustrated in Fig. 2. All these statements on the positions of the levels are surely true as long as the important term for bonding is the so-called Hund resonance integral, which is the off-diagonal matrix element connecting the central and attached portions. Since diagonal sums are unaffected by the addition of off-diagonal elements, it follows that the sum of the two roots of the quadratic must equal an energy level of the free central atom, plus one of the attached atom. Hence if one root is lowered in virtue of the resonance integral, the other must be raised.

Let us now discuss the case of $\text{Fe}(\text{CN})_6^{3-}$. We can consider each CN radical as contributing one electron (*viz.*, the electron which corresponds to a $2p\sigma$ wave function directed towards the central atom). There are thus 17 electrons in all to house (apart from completed inner shells). Twelve electrons can be housed in the lower roots of the secular equations associated with (2)–(7), since the Pauli principle allows two electrons to an orbital state. The remaining five electrons are then to be accommodated in the three nonbonding, i.e., purely central $d\epsilon$ orbitals, which are preferable to antibonding states. One, and only one, of these five electrons can have a private orbital, and so only one spin contributes to the susceptibility. With $\text{Fe}(\text{CN})_6^{4-}$, the last six electrons are snugly accommodated in the three $d\epsilon$ levels, and so there is diamagnetism. Of course, if the bonding action is weak enough, several electrons may prefer to occupy private orbitals, even though antibonding, in order to secure large spin and low internal energy for the central atom. This is a refinement not included in the crude forms of the method of molecular orbitals, for it is the interelectronic exchange energy, not incorporated in the one-electron problem, which is lowered by making the spins parallel. Thus we see that, as in the other methods, the susceptibility will have the low values characteristic of the cyanides only if the bonding action is larger than the Russell-Saunders structure of the central atom.

COMPARISON OF THE VARIOUS METHODS

We have now seen that all three descriptions are capable of explaining the anomalously low

¹⁷ Cf. also J. H. Van Vleck and A. Sherman, *Rev. Mod. Phys.* **7**, 218–222 (1935).

magnetism of the cyanides. The question naturally arises as to which corresponds the closest to reality. It seems to us that in the cyanides one must decide in favor of III or possibly I. One reason is that method III is the most general, since it is noncommittal on the amount of polarity, which can be anything between $\text{Fe}^{3+}(\text{CN})_6^-$ and $\text{Fe}^{9-}(\text{CN}^+)_6$, depending on the size of the coefficients α , β , γ . In fact, II can be regarded as a special case of III, wherein these coefficients are zero and the CN orbitals have lower energies than those of the central atom, so that the twelve electrons digested by (2-7) are located on the CN radicals. Method I is also to a certain extent a special case of III, corresponding to

$$\alpha = \beta = \gamma = \sqrt{\frac{1}{2}}, \quad (8)$$

but we have seen in the preceding paper that in any event I differs from III in assuming localized or unidirectional bonds. Eq. (8) may be regarded as the condition for ideal covalency, as when it is satisfied, the twelve bonding electrons spend equal amounts of time on the $(\text{CN})_6$ group and on the central atom. The actual behavior is not as extreme as in (8), for the structure $\text{Fe}^{3-}(\text{CN})_6$ given by (8) requires too much negative charge on the Fe ion, as mentioned at the beginning of the preceding paper.

A decision between II and III is furnished by the fact that $(\text{NH}_4)_3\text{FeF}_6$ obeys the ordinary formula (1), and so has a much higher magnetism than $\text{K}_3\text{Fe}(\text{CN})_6$. Now it is known from other evidence¹⁸ that $(\text{NH}_4)_3\text{FeF}_6$ is much more polar in its structure, i.e., more nearly $(\text{NH}_4^+)_3\text{Fe}^{3+}(\text{F}^-)_6$, than is $\text{K}_3\text{Fe}(\text{CN})_6$. With the method of the crystalline potential, the fields responsible for the Stark splitting are those due to the negative charges surrounding the paramagnetic cation. Hence if method II were always applicable, the quenching of magnetism would be more complete in the fluoride than in the cyanide, contrary to experiment. On the other hand, in the method III of molecular orbitals, the strength of the bond or separation of the levels stands in no immediate relation to the amount of polarity, and it is perfectly possible to have a covalent structure quench magnetism

more completely than an ionic one. In fact, if the resonance integrals are the determining factor in chemical bonds, one comes nearer to (8) the greater the interatomic forces available to suppress the magnetism.

Pauling has argued that the suppression of magnetism is evidence in favor of the electron pair mechanism I in $\text{Fe}(\text{CN})_6^{3-}$. However, we have seen that II or III can also be effective in quenching magnetism, so that it does not seem possible directly to infer the bond type from magnetic behavior. We agree with Pauling that covalent bonds are more effective in destroying magnetism than ionic, but the reasoning by which we reach this conclusion is somewhat different and is based on the empirical comparison of $(\text{NH}_4)_3\text{FeF}_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ made above. Once it has been established empirically in a few cases that covalent bonds destroy magnetism more than ionic, one is probably justified in extrapolating to other cases, and supposing the bonds to be covalent when most of the magnetism has been destroyed.

If method III is to be preferred to II, the calculations of Schlapp and Penney,⁸ based ostensibly on II, must be given a somewhat different interpretation than previously. They by no means lose applicability, for they are based largely on the symmetry group properties, and so retain practically as much significance with III as with II, except that the size of the crystalline potential is not to be taken too literally. The splittings of a few volts may now relate to the magnitude of the Hund resonance integrals rather than of the crystalline potential, but remain comparable to the Russell-Saunders structure, making it still reasonable that one should sometimes have the cyanide behavior and sometimes the sulphate.

One feature which is common to methods I, II, III is that nickel salts should have a susceptibility corresponding to $S=1$ rather than to $S=0$ in (1) even if the cubic splitting is large compared with the Russell-Saunders structure. This statement is true if the grouping about the nickel ion is either tetrahedral or octahedral. The demonstration has been given by Pauling² with mechanism I and by Van Vleck and Sherman¹⁷ with III. If II is used, one has only to note that Ni^{++} has two more electrons than Fe^{++} , so

¹⁸ L. Pauling, J. Am. Chem. Soc. **54**, 988 (1932); Pauling and Huggins, reference 2.

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.