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Theory of the Variations in Paramagnetic Anisotropy Among Different Salts of the Iron Group

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A theoretical explanation is given of why nickel salts are nearly isotropic magnetically, while those of cobalt exhibit over 25 percent anisotropy even though the Ni^{++} and Co^{++} ions are both in F states and are adjacent in the periodic table. The cause is an inversion of the levels in the crystalline Stark effect in passing from the configuration $d^8\,{}^3F$ (Ni^{++}) to $d^7\,{}^4F$ (Co^{++}). If the crystalline field has only rhombic symmetry, but with the deviations from cubic symmetry comparatively small, extension of the methods in Penney and Schlapp's preceding paper shows that a nearly isotropic level will be the ground level in Ni^{++}, but an anisotropic one in Co^{++}. It is to be particularly noted that the inversion exists purely in virtue of the difference between the configurations d^7 and d^8, and does not require different crystalline fields in Ni and Co compounds. The theory predicts that hydrated Ni salts conform closer to Curie's law than those of Co, and have a Curie constant more nearly equal to the "spin only" value $4NS(S+1)(he/4\pi mc)^2/3k$. This agrees with experiment. Other pairs of ions are cited in the iron group in which the inversion phenomenon is encountered, with attendant diversity in magnetic behavior. The nearly perfect magnetic isotropy of manganous salts is trivial, as the ground state of Mn^{++} is ${}^6S$; the slight anisotropy may be due to a small amount of incipient j-j coupling or to distortion of the constancy of orbital angular momentum by the crystalline field, so that the orbital magnetic moment does not vanish completely in S states.

NO ONE who has examined the measurements of the principal susceptibilities of salts of the iron group can fail to note how remarkably the amount of magnetic anisotropy varies with the nature of the cation. Typical determinations are, for instance, those by Rabi,[1] according to which the ammonosulphates of Mn, Co, Ni, and Cu exhibit anisotropies amounting respectively to 1, 30, $1\frac{1}{2}$, 20 percent.

The nearly perfect isotropy of the manganous salts is exactly what one expects inasmuch as the Mn^{++} ion has a ${}^6S$ ground state. Nearly complete symmetry should also be found in ferric salts, as Fe^{+++} and Mn^{++} have the same configuration, but adequate data on ferric compounds are wanting. The usual cause of magnetic anisotropy is the unsymmetrical partial freezing of orbital angular momentum by the lattice forces. The orbital magnetism is thus largely destroyed by these forces, but not completely. Particularly important is usually the coupling between the spin and the remains of the orbital angular momentum, which are not centro-symmetric and so destroy the equivalence of different spin orientations. In S states with perfect Russell-Saunders coupling there is no orbital angular momentum to congeal, and so the usual cause of anisotropy disappears in manganous salts. The ordinary explanation of the small residuum (about 1 percent) of anisotropy found in

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[1] I. I. Rabi, Phys. Rev. **29**, 173 (1927).

manganous compounds is the magnetic spin-spin coupling, since the electrostatic exchange coupling is well known not to cause anisotropy. However, it seems doubtful whether the magnetic spin-spin forces could be great enough to cause even the 1 percent dissymmetry in manganous salts of high "magnetic dilution," such as e.g., hydrated sulphates, where the separation of the paramagnetic ions is great. Therefore we wish to suggest the possibility of a small amount of incipient j-j coupling, not enough to distort appreciably the g-factors from their Russell-Saunders values, but enough to impart a slight amount of orbital angular momentum to S states which would then behave anisotropically. Along with this is also, perhaps more important, the angular momentum which arises because the crystalline fields do not have complete central symmetry. In quantum mechanics the orbital angular momentum cannot be constant in time in noncentral fields[2] and so cannot vanish completely in the presence of the latter.

So much for the rather straightforward case of Mn. Much more puzzling is the great difference in isotropy between nickel and cobalt salts. The ions Co^{++} and Ni^{++} are adjacent in the periodic table, and both are in F states (respectively $d^7\,{}^4F$ and $d^8\,{}^3F$). Nevertheless Ni salts are nearly as isotropic as those of Mn, while Co salts are the least symmetrical of the whole group. Closer examination reveals that precisely this behavior is to be expected if the crystalline field possesses only rhombic symmetry, but with the departures from cubic symmetry relatively small. The development of the crystalline potential then takes the form

$$V = \sum_i [f(r_i) + Ax_i^2 + By_i^2 - (A + B)z_i^2 + D(x_i^4 + y_i^4 + z_i^4)], \qquad (1)$$

provided we neglect the departures from cubic symmetry in the fourth but not the second order terms. The summation need be extended for our purposes only over the electrons not in closed shells, i.e., the d electrons in the ions of the iron group, inasmuch as completed shells exhibit no orientation effect and so contribute nothing interesting to (1). The reader is referred to the preceding paper by Penney and Schlapp and to reference 3 in case he desires further general exposition of the use of crystalline potentials in connection with magnetic problems.[3] That the rhombic or second order part of (1) is subordinate to the cubic or fourth order part is evidenced by the fact that paramagnetic salts are nearly isotropic in many cases, and especially by the success which has attended Penney and Schlapp's preceding calculation of the temperature dependence of the susceptibilities of rare earth salts involving Nd and Pr under the assumption that only the cubic portion of (4) need be considered. They have also tried calculations keeping only the rhombic part of (1), but the wrong temperature dependence is then obtained in the rare earths, as well as far too much anisotropy in Ni salts.

If the "cubic" or fourth-order part of (1) is the dominant noncentral term, then from Bethe's[4] group theory of levels in crystalline fields, one finds that

[2] Cf. J. H. Van Vleck, Phys. Rev. **31**, 600 (1928).

[3] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," section 73.

[4] H. Bethe, Ann. d. Physik **3**, 133 (1929); especially pp. 164–167, 196–199.

the Stark splitting is arranged either as in Fig. 1, or as in this figure turned upside down. The vertical lines represent the matrix elements of magnetic moment along some one principal direction, say x. The separation of the components of Γ_4 or of Γ_5 is due only to the rhombic terms, since Γ_4, Γ_5 (in Bethe's notation) are triply degenerate "Darstellungen" in strictly cubic fields.

If Fig. 1 is right side up, the orbital magnetic moment will be largely suppressed, and its "remains" will be nearly isotropic for the following reason. By perturbation theory,[5] the magnetic moment induced in the state a by application of a magnetic field H along x is given by the expression

$$2H \sum_k \left| \mu_x(ak) \right|^2 / h\nu(ka), \tag{2}$$

where the $\mu(ak)$ are the matrix elements of magnetic moment in the absence of H but in a system of representation which diagonalizes (1). The matrix μ will contain no diagonal elements, because, as the writer has shown elsewhere,[3] crystalline fields of no more than rhombic symmetry suppress the diagonal elements of orbital angular momentum (neglecting perturbations by spin-orbit interaction, which restores some of the diagonal part in systems with an odd number of electrons). In the case shown in Fig. 1, the summation over k embraces only c and f, but if one changes the direction of H to another principal axis y or z, one encounters the matrix elements of μ_y, μ_z and these may join a to other components of Γ_4 and Γ_5 than c and f. One finds that the magnetic anisotropy of a exists only in virtue of the difference between the frequencies $\nu(ab)$, $\nu(ac)$, $\nu(ad)$ or between $\nu(ae)$, $\nu(af)$, $\nu(ag)$, and these percentage differences are small since the rhombic is small compared to the cubic separation.

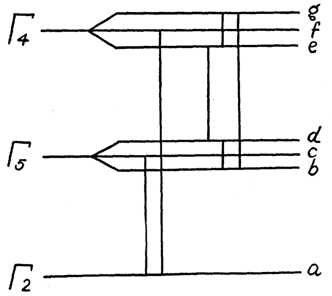

Fig. 1.
(upright in Ni^{++}, inverted in Co^{++})

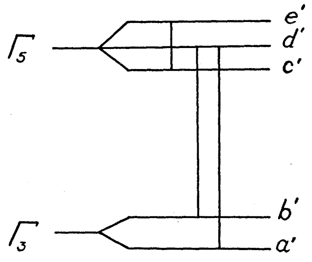

Fig. 2.
(upright in Cu^{++}, inverted in Fe^{++})

Let us, however, turn Fig. 1 upside down, and suppose that the separations e-f-g, though small compared to a-e, etc., are nevertheless large compared to kT, making only g a normal state. The orbital magnetic moment will then be much less completely quenched than without the inversion, since

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[5] See, for instance, p. 145 of reference 3.

the denominators $\nu(ge)$, $\nu(gf)$ will be involved in the formula analogous to (2). Furthermore there will be vastly more anisotropy than without the inversion. This will be true not merely because the percentage difference between $\nu(ge)$ and $\nu(gf)$ is greater than that between $\nu(ab)$ and $\nu(ac)$ or $\nu(ad)$ but also because the full symmetry of moment in the limiting case of perfectly cubic fields is achieved only with equal distribution of atoms among the three components of Γ_4 rather than concentration purely in one component g.

It is clear that one can understand the difference between Ni^{++} and Co^{++} if one can justify turning Fig. 1 upside down in passing from one of these ions to the other. Now it actually turns out that for a *fixed* sign of A, B, D in (1), precisely this behavior is to be expected theoretically. The argument is as follows. Let us consider matrix elements in the L, M_L system of representation rather than in the final system which diagonalizes (1). Then from the properties of the rotation group Penney and Schlapp find in the preceding paper that, regardless of the number n of electrons in the incomplete shell the matrix elements of $\sum(x_i^4+y_i^4+z_i^4)$ are of the form

$$\sum_i(x_i^4 + y_i^4 + z_i^4)(LM_L; LM_L) = Qf(L, M_L) + 3n\overline{r^4}/5, \tag{3}$$

where Q depends on L, S, n but not on M_L, and where

$$f(L, M_L) = M_L^2(7M_L^2 - 6L^2 - 6L + 5) + 3L(L^2 - 1)(L + 2)/5. \tag{4}$$

Besides (3) there are also elements of the form $\Delta M_L = \pm 4$ proportional to Q, as well as elements nondiagonal in L, but the explicit form of these does not concern us. Our interest is in the sign of the proportionality factor Q, which can be determined by the following adaptation of the Goudsmit-Slater method[6] of diagonal sums. For the configuration d^8, the only arrangement in m_l, m_s quantization consistent with $M_L=\sum m_l=3$, $M_S=\sum m_s=1$ is $m_l=2$, $m_l=1$, $m_l=0$ each twice, $m_l=-1$, $m_l=-2$ each once. The spur invariant for $M_L=3$, $M_S=1$ thus consists of but a single term, which yields a ^3F state. Hence, since f is even in M_L,

$$Q(d^8\,{}^3F)\cdot f(3, 3) = Q(d^2D)\,[3f(2, 2) + 3f(2, 1) + 2f(2, 0)]. \tag{5}$$

Here $Q(d^8\,{}^3F)$ means the value of Q appropriate to the configuration $d^8\,{}^3F$, while $Q(d\,{}^2D)$ of course relates to a single isolated d electron. The term in $\overline{r^4}$ has been omitted since it is invariant of the vector addition involved in constructing the Russell-Saunders coupling. For the case $M_L=3$, $M_S=3/2$ of d^7, one has the same arrangement of m_l's as before, except that $m_l=0$ is filled only once, and consequently

$$Q(d^7\,{}^4F)f(3, 3) = Q(d^2D)\,[3f(2, 2) + 3f(2, 1) + f(2, 0)]. \tag{6}$$

On comparing (5) and (6) and noting that

$$2f(2, 2) + 2f(2, 1) + f(2, 0) = 0, \tag{7}$$

one sees that $Q(d^8\,{}^3F)$ is the negative of $Q(d^7\,{}^4F)$. Of course the diagonal ele-

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[6] S. Goudsmit, Phys. Rev. **31**, 945 (1928); J. C. Slater, *ibid.* **34**, 1293 (1929).

ments (3) are not the same as the characteristic values of $\sum(x_i^4+y_i^4+z_i^4)$, but except for the difference in Q, the matrix representing this expression in the L, M_L system is the same for $d^8\,{}^3F$ as $d^7\,{}^4F$ inasmuch as L is the same in both cases. Hence the characteristic values are obtained by the same canonical transformation and differ merely in the proportionality factor Q, which will thus cause inversion in the passage from Ni to Co. It is particularly gratifying that alteration of the sign of D in (1) is thus not necessary to invert the crystalline Stark effects. The crystals of Ni and Co hydrated sulphates, etc. have presumably so nearly the same structure and ionic arrangement that it would be illogical, to say the least, to postulate radically different fields in the two cases.

In the foregoing we have neglected entirely the spin in the interest of simplicity. Actually the spin is the main cause of the paramagnetism in Ni and Co, though not of its anisotropy. In point of fact, the spin-orbit interaction is comparable with the effect of the rhombic dissymmetry, but is subordinate to the "cubic" term, so that the inversion of cubic levels still comes into play. Inclusion of the spin-orbit interaction makes the remains of the orbital magnetic moment contribute to the part of the susceptibility which is inversely proportional to temperature, rather than merely a term such as (2) which is independent of temperature. When Fig. 1 is right side up, the spin interacts effectively with a smaller and more isotropic orbital moment than when Fig. 1 is inverted. The most potent elements of μ in the spin-orbit coupling, which is much looser than in the free gaseous state, can be shown[3] to be those whose associated frequencies $\nu(ij)$ are small. Hence the departures of the Curie constant C from the Stoner-Bose "spin only" value

$$C = 4NS(S+1)(he/4\pi mc)^2/3k \tag{8}$$

should be larger in Co than in Ni salts, and deviations from Curie's law in highly hydrated salts should appear at higher temperatures with a Co than with a Ni cation. (The hydration is to avoid exchange coupling between atoms.) This agrees with experiment. The deviation from (8) is about 30 percent in the nickel sulphates, as compared with 70 percent in those of cobalt. Further calculations by Schlapp and Penney, to appear shortly, predict that in hydrated nickel salts the deviations should become important only at temperatures near liquid helium. This is confirmed by Gorter, de Haas, and v. d. Handel's recent remeasurement[7] of $NiSO_4 \cdot 7H_2O$ at low temperatures (down to liquid hydrogen) which has obliterated Jackson's previous large negative Δ and restored Curie's law almost perfectly. On the other hand, $CoSO_4 \cdot 7H_2O$ apparently demands a Δ of about 14 in the Weiss-Curie formula $\chi = C/(T+\Delta)$, although it must be cautioned that here new measurements are not available.

By arguments very similar to the previous, one can show that the inversion phenomenon should also be found in the pair Fe^{++}, Cu^{++}, respectively $d^6\,{}^5D$ and $d^9\,{}^2D$, and also pairs of ions reciprocally related on the left and right sides of the group, such as (Cr^{+++}, Co^{++}) or (Ni^{++}, V^{+++}). We call ions re-

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[7] C. J. Gorter, W. J. de Haas, and J. v. d. Handel, Leiden Comm. 218d.

ciprocally related if they have respectively x and 10-x d electrons, since then their ground states have the same L, S.

Adequate data are wanting on single crystals of Cr and V salts, but the Curie constant does have much more closely the Stoner-Bose value (8) for Cr^{+++} than for Co^{++}, as one should expect from the foregoing. In $Cr_2(SO_4)_2 K_2SO_4 \cdot 24H_2O$ the deviation from (8) is only about 2 percent.[8] The variation in the applicability of (8) is thus even more pronounced in the pair Cr^{+++}, Co^{++} (2 *vs.* 70 percent deviation) than in the pair Co^{++}, Ni^{++} (70 *vs.* 30). This is understandable on the ground that the multiplet structure and hence the spin-orbit interaction for the free ion are considerably smaller in Cr^{+++} than in Co^{++} or Ni^{++}. Of course the departures from (8) will be greater the larger this interaction, all other circumstances being equal. Consequently the alteration in free multiplet width and the inversion phenomenon reinforce each other in accentuating the deviations from (8) in Co^{++} as compared to Cr^{+++}.

The pair Fe^{++}, Cu^{++} require rather careful examination. Here we encounter D rather than F levels. Now Bethe[4] has proved that D terms split under the potential (1) in the fashion shown in Fig. 2, where the separation of the components of Γ_3 or of Γ_5 is due entirely to the deviations from cubic symmetry occasioned by the rhombic terms. The first thing to be remarked is that Fig. 2 is upright in Cu^{++} and inverted in Fe^{++} if Fig. 1 is upright in Ni^{++}. This follows from the fact that $Q(d^9\ {}^2D)$ has the opposite sign from $Q(d^8\ {}^3F)$ inasmuch as by the method of diagonal sums

$$Q(d^9\ {}^2D)f(2,2) = Q(d^2D)\left[3f(2,2) + 4f(2,1) + 2f(2,0)\right] = -\ Q(d^2D)f(2,2), \quad (9)$$

and by (4) the bracketed sum in (9) has the value $-12/5$ as compared with $36/5$ for the corresponding bracketed sum in (5). Bethe[4] has shown that for a fixed sign of Q, as in a one electron system, the D level requires inversion of Fig. 2 if the F level requires an upright Fig. 1. When the sign of Q changes, there are thus two cancelling inversions which together leave Fig. 2 upright.

To be consistent with our interpretation of Ni and Co, it thus appears[9]

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[8] W. J. de Haas and C. J. Gorter, Leiden Comm. 208c.

[9] At this juncture it is perhaps well to remark that the reversal of the sign of Q is perhaps a more general and certain phenomenon for the pairs Ni^{++}, Co^{++} and Fe^{++}, Cu^{++} than for the pair Ni^{++}, Cu^{++}. The reversal for the former pair is contingent only upon (7) and hence takes place for any potential whose diagonal elements vanish when summed over M_L except for an additive constant, such as $3n\overline{r^4}/5$ in (3), which is independent of the type of vector addition. That the additive constant is indeed independent of the vector compounding is shown by the theorem (cf. Niessen, Phys. Rev. **35**, 274 ff., 1929) that $\Sigma_{M_L} F(n_1 n_2 \cdot\cdot\ M_L;\ n_1 n_2 \cdot\cdot\ M_L) = (2L+1) \times \overline{F}(n_1 n_2 \cdot\cdot\ ;\ n_1 n_2 \cdot\cdot\ )$ where the matrix elements relate to any function $F(r, \theta, \phi)$ of polar coordinates and $4\pi\overline{F} = \iint F \sin\theta d\theta d\phi$ .The function $\overline{F}$ is a purely radial one and consequently invariant of the vector addition involved in Russell-Saunders coupling etc. Hence the Ni^{++},Co^{++} inversion is surely found for other forms of potential besides (1), and the great diversity in anisotropy in this pair requires only that the crystal symmetry be dominantly but not completely cubic. On the other hand after Eq. (9) explicit use was made of the numerical form (4) of the matrix elements of the fourth degree part of (1) in proving the reversal in the sign of Q for the pair Ni^{++}, Cu^{++}. It is hence conceivable, though improbable, that if the cubic potential requires large sixth, eighth, etc. degree terms for its representation in addition to the fourth order terms, the reversal in the sign of Q may exist for the Ni^{++}, Co^{++} and Cu^{++}, Fe^{++} pairs, but not for Ni^{++}, Cu^{++}. Fig. 2 would then be upright in Fe^{++} and inverted in Cu^{++}.

necessary that Fig. 2 be upright in Cu^{++} and inverted in Fe^{++}. Now Bethe[4] has demonstrated that the portion Γ_3 of Fig. 2 is "nonmagnetic," and so μ consequently has no matrix elements of the form $\mu(a'b')$, whereas the elements inside Γ_5 do not all vanish. The expression analogous to (2) will consequently be much larger in Fe^{++}, where e' is a ground state, than in Cu^{++}, because of the existence of small denominators such as $\nu(e'c')$. Hence the remains of the orbital angular momentum will be larger in Fe^{++} than Cu^{++}, and, all other things being equal, the distortion from (8) with attendant magnetic anisotropy should be much more accentuated in Fe^{++} than in Cu^{++}. Actually the anisotropy of cupric salts (e.g., 26 percent in $CuK_2(SO_4)_2 \cdot (6H_2O)$ is usually greater than for ferrous ones (e.g., 16 percent in $FeK_2(SO_4)_2 \cdot 6H_2O$), while (8) holds no more closely for Cu^{++} than for Fe^{++}. About 20 percent deviations from (8) are found in both cases. Because of the somewhat greater anisotropy in the cupric case, it thus appears at first sight that the inversion of Fig. 2 comes at the wrong place. However, "all other things" are not equal. The free multiplet structure is wider for Cu than Fe, so that if there were no inversion the spin-orbit distortion would be bigger in Cu than in Fe. Also the spin quantum number has the small value 1/2 in Cu^{++}, compared with 2 in Fe^{++}, so that residual orbital angular momentum of given magnitude is relatively more important in Cu^{++} than in Fe^{++}. These two effects may more than counteract the fact that the denominators in the formula for the induced orbital moment are smaller in Fe^{++} than in Cu^{++}. One thing to be particularly emphasized in connection with the question of anisotropy is the following. The orbital moment induced in a' in Fig. 2 exists, to be sure, solely in virtue of the matrix element $\mu(a'c')$, $\mu(a'd')$, $\mu(a'e')$ rather than $\mu(a'b')$, and hence tends to be small because the frequencies $\nu(a'c')$ etc. are large. However, unlike the case of a in Fig. 1, this moment in a' does not owe its anisotropy purely to departures of the ratios $\kappa = \nu(a'c')/\nu(a'd')$ etc. from unity. Instead the full cubic isotropy of the induced moment in Γ_3 is achieved only when the two components of Γ_3 are equally populated, whereas we suppose the separation $a' - b'$ large compared to kT, so that only a' is inhabited. Consequently, the anisotropy in the induced orbital moment of a', Fig. 2 is of the order of magnitude unity, like that of g in Fig. 1 or e' in Fig. 2, whereas that in a, Fig. 1 is only of the order $\kappa - 1$. By an anisotropy of the order unity we mean that the differences between the x, y, z components are comparable with the components themselves. Of course the anisotropy is in any case diminished because the residual orbital angular momentum is overshadowed by the spin, but we can say that for given deviations from (8), the anistropies should be of the same order of magnitude regardless of whether or not Fig. 2 is inverted, and inversion accentuates the anisotropy only in so far as the deviation from (8) is enhanced, whereas we have seen that in the Fe^{++}, Cu^{++} pair there are other counteracting tendencies which forestall this enhancement. The effect of inversion on anisotropy is thus a different story for Fig. 2 than Fig. 1. It must be further remembered that Fe, Cu are not adjacent in the periodic table, and their salts' crystalline fields need not resemble each other as closely as those of Co, Ni, thus obscuring the purity of the inversion phenomenon. The inversion becomes less important the more one increases the rhombic terms at the expense of the cubic ones.

In order to make Figs. 1, 2 upright at Ni^{++}, Cu^{++} respectively rather than Co^{++}, Fe^{++}, it is necessary that the constant D in (1) be positive. This follows since the quotient of the bracketed sum in Eq. (5) and $f(3, 3)$ is positive, making Q have the same sign in Ni^{++} as for a one electron system, where Bethe[4] shows that Fig. 1 is upright if D is positive. The positive choice of D agrees with Penney and Schlapp's preceding calculations on the susceptibilities of the rare earths, but iron and rare earth salts are so widely different that it seems scarcely necessary that the sign of D be the same in both cases.

Detailed numerical calculations amplifying and testing quantitatively the foregoing ideas will be published by Schlapp and Penney and by Jordahl. The writer wishes to thank them for valuable discussions and comments.