

## The Influence of Crystalline Fields on the Susceptibilities of Salts of Paramagnetic Ions. I. The Rare Earths, Especially Pr and Nd

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The paramagnetic susceptibilities of the salts of the rare earth elements Pr and Nd are considered on the assumption that it is permissible to represent the potential of the electric field of the atoms surrounding the metallic ion by a Taylor's expansion. This amounts to applying to the whole crystal the method of the "self-consistent field," and consequently neglects exchange effects between different crystal atoms. Hund has calculated the susceptibilities on the assumption that the ion can be regarded as free and that the multiplet intervals are so large compared with  $kT$  that only the lowest level need be considered. The introduction of an electric field causes a splitting of the levels and a redistribution of magnetic moment, with a consequent change in the susceptibility. The theoretical interpretation of the Curie-Weiss law  $\chi = C/(T + \Delta)$  is considered. At temperatures so high that  $kT$  is large compared with the splitting produced by the crystal field, the susceptibility can be expanded in the form of a series of inverse powers of  $T$ . It is shown that the susceptibility of a crystal powder, or the average susceptibility over all directions in a single crystal is of the form  $\chi = C/T + C_2/T^3 + \dots$  the term in  $1/T^2$  vanishing rigorously. Thus at sufficiently high temperatures, the susceptibility of a crystal powder obeys the simple Curie law up to and including terms in  $1/T^2$ . However, the curious result emerges that at ordinary temperatures  $kT$  is of the same order as the energy separations produced by the crystal field, and the behaviour of the susceptibility actually simulates the Curie-Weiss law closely over a large range of temperatures. The hydrated sulphates of Pr and Nd are considered in detail. Excellent agreement is obtained with the experimental results of Gorter and de Haas for the variation of susceptibility with temperature on the assumption that the crystal field has cubic symmetry, and can be represented by a potential  $D(x^4 + y^4 + z^4)$ . In this connection the matrix elements of the squares and fourth powers of the coordinates for a many-electron system are given. The over-all splitting produced by this field in the hydrated sulphates is  $389 \text{ cm}^{-1}$  for Pr and  $834 \text{ cm}^{-1}$  for Nd, the detailed appearance of the energy spectrum being shown in Fig. 1. A comparison of the constant  $D$  in the two cases gives a value for Nd nearly four times that for Pr.

THE theory of paramagnetic susceptibilities as developed by Van Vleck<sup>1</sup> and others has been applied with considerable success to the calculation of the Curie constants of salts of the rare earth group on the assumption that it is legitimate to regard the metallic ion as free. At ordinary temperatures, the theory then leads to an expression for the susceptibility of the Curie form  $\chi = C/T$ . Experimentally the Curie-Weiss law

$$\chi = C/(T + \Delta), \quad (1)$$

where  $\Delta$  is a constant over a wide range of temperature, frequently gives a good representation of the results. It very often happens that at extremely

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<sup>1</sup> J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford, 1932.

low temperatures, neither law will fit the experimental measurements. It has been suggested<sup>2</sup> that the deviations from the simple Curie law are due to the influence of the electric fields of the surrounding ions, which remove, wholly or partially, the spatial degeneracy of the energy levels of the free ion, thereby modifying both their positions and magnetic moments. Fields of this nature have already been postulated by Becquerel<sup>3</sup> and by Kramers,<sup>4</sup> in connection with the Zeeman effect and paramagnetic rotation in crystals, while Bethe<sup>5</sup> has worked out by group theory the energy spectrum of ions in fields of various symmetries. In an ionic crystal, such as nickel chloride, it seems likely that the crystal field will have the same symmetry as the crystal, but in a molecular crystal, such as hydrated  $\text{Pr}_2(\text{SO}_4)_3$ , there is no reason why this should any longer be true. In the absence of definite knowledge of the electric field to which an ion in a given crystal is subject, the only possible procedure is to find the simplest field which will give agreement with the experimental results.

Although considerable experimental material is available, it is not as complete as could be desired; in particular, accurate measurements at different temperatures on single crystals are lacking. From the calculations given below, there seems to be no doubt that the mechanism of crystal fields is competent to account for all the observed results. A summary of the results obtained for Pr, Nd, Ni, and Cu has been given in a Letter to the Editor.<sup>6</sup> In the present paper an attempt is made to calculate the magnitude of the electric fields necessary to account for the experimental variation with temperature of the susceptibility of the rare earth elements Pr and Nd. In a second communication we shall present the calculations for Ni, Co and Cr while those for Cu will be given by Mr. Jordahl. We have considered only crystals of high magnetic dilution. This is necessary in order that the influence of exchange may be neglected. It has been found possible in these cases to represent the variation of susceptibility over a wide range of temperature by an equation of the form (1) although as will be discussed more fully below, this arises in a peculiar way, and also to account for the deviations from (1) which occur at very low temperatures.

The majority of measurements have been made on crystal powders, so that the observed value of  $\Delta$  represents an average over all the directions in a single crystal. In such cases, the simplest assumption is that of a cubically symmetric field, and this involves only a single parameter which must be chosen to fit the experimental average  $\Delta$ . With Pr and Nd it proves that a cubic field is adequate to account for all the features which have been observed up to the present. It is possible to fit the experimental curves very

<sup>2</sup> Reference 1, Chap. IX.

<sup>3</sup> J. Becquerel, *Zeits. f. Physik* **58**, 205 (1929).

<sup>4</sup> H. A. Kramers, *Proc. Amst. Acad.* **32**, 1176 (1929).

<sup>5</sup> H. Bethe, *Ann. d. Physik* **3**, 133, (1929); *Zeits. f. Physik* **60**, 218, (1930).

<sup>6</sup> O. M. Jordahl, W. G. Penney and R. Schlapp, *Phys. Rev.* **40**, 637 (1932). The affix +++ for Pr and Nd, and ++ for Ni, Co, Cu, is to be understood throughout where the symbol of the element refers to the ion.

well, but owing to a discrepancy of some 16 percent in the absolute magnitude of the susceptibility as measured by different observers,<sup>7</sup> more refined calculations seem out of place. However, when more detailed experimental data are available it may be necessary to introduce fields of lower symmetry to obtain agreement with experiment.

One may classify crystal fields as strong or weak according as they are able or unable to break down the coupling between the total orbital and spin angular momenta. It is assumed that the fields are never strong enough to break down the coupling between the individual orbital or individual spin angular momenta. Thus the crystal field is strong or weak according as it produces a splitting of energy levels which is large or small compared with the multiplet separation. The criterion that the ion can be considered as free is that the work required to turn over the ion against the influence of the crystal field should be small compared with  $kT$ . For the rare earths, it has been shown that the magneton numbers calculated on the assumption that the ions are perfectly free agree closely with the observed values, indicating that the crystal fields are weak. For the iron group, on the other hand, the fields are so strong that the contribution of the orbital angular momentum to the susceptibility is very much less than it would be for the free ion, although the spin may still contribute its full amount. This difference in the crystal fields is in harmony with the fact that in the rare earths the  $4f$  electrons causing the paramagnetism are much more completely screened from outside influences than the  $3d$  electrons of the iron group. Our quantitative results are in excellent accord with the theory of Van Vleck and it was at his suggestion that the detailed calculations given in this paper were made with the object of testing numerically the general predictions of the theory.

#### THE CONSTANT $\Delta$ FOR THE RARE EARTHS

The fundamental expression for the susceptibility is

$$\chi = -\frac{N}{H} \sum \frac{\partial W}{\partial H} e^{-W/kT} / \sum e^{-W/kT}, \quad (2)$$

the summation extending over all levels. Here  $H$  is the magnetic field,  $N$  Avogadro's number, and  $W$  the energy levels in the presence of the magnetic field. Let us assume that a certain number of the levels form a group having a range of energy much smaller than  $kT$ , while the other levels are all so far distant that on account of the Boltzmann factor, their contribution to the susceptibility can be neglected. This state of affairs would presumably be realized in the rare earths at high temperatures, the "low-frequency" group comprising the components into which the lowest multiplet level is split by the crystal field, the components of the other multiplets being much higher. Let us take as origin the center of gravity of the low frequency group. Then,

<sup>7</sup> The magneton numbers for the salt  $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  at room temperatures according to different observers are as follows: Cabrera 18.00, Gorter and de Haas 16.68, Zernicke and James 17.50. The susceptibility is proportional to the square of the magneton number.

if we neglect saturation, i.e., retain only the part of  $\chi$  independent of  $H$ , we find

$$\chi = C/T + C_1/T^2 + \dots$$

where

$$C = N \sum \frac{\partial W^2}{\partial H} / 2kH(2J + 1), \quad C_1 = -N \sum \frac{\partial W^3}{\partial H} / 6H(2J + 1)$$

Thus to the approximation which neglects terms in  $1/T^3$  and beyond, the constant  $\Delta$  in the empirical formula (1) is given by

$$k\Delta = \frac{1}{3} \sum \frac{\partial W^3}{\partial H} / \sum \frac{\partial W^2}{\partial H}.$$

We shall now show that under the assumptions stated above the value of the constant  $C$  is independent of the direction of the magnetic field, and that the susceptibility averaged over three perpendicular directions follows the law  $\chi = C/T + C_2/T^3 + \dots$  the term in  $1/T^2$  being absent. The Hamiltonian is of the form  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' + H\mathcal{H}_1$  where  $\mathcal{H}_0$  is the Hamiltonian of the free ion,  $\mathcal{H}'$  is the potential of the crystal field, and  $\mathcal{H}_1$  is the component of the magnetic moment  $\beta(L + 2S)$  in the direction of the magnetic field. Using the property of the invariance of the spur we have

$$\sum \partial W^2 / \partial H = \text{Sp}(\partial / \partial H)(\mathcal{H}_0 + \mathcal{H}' + H\mathcal{H}_1)^2.$$

The spur of  $(\mathcal{H}_0 + \mathcal{H}')\mathcal{H}_1$  vanishes, since the terms contributing to this spur have equal and opposite values for  $\pm M$ , so that the above expression is equal to  $2H\text{Sp}\mathcal{H}_1^2$ . Here Sp denotes summation over the elements diagonal in a given value of  $J$  and in all possible values of  $M$ . Since the multiplet width is large compared with  $kT$  we are concerned only with those elements of the magnetic moment  $\mathcal{H}_1$  which are of the low frequency type, i.e., diagonal in  $J$ , the contribution of the off-diagonal elements to the susceptibility being independent of the temperature. Now  $\text{Sp} \mathcal{H}_1^2 = g^2\beta^2 J(J+1)(2J+1)/3$  so that the constant  $C$  has the Hund value  $Ng^2\beta^2 J(J+1)/3k$  for all directions of the magnetic field.

The value of  $C_1$  for a crystal powder is the average of the three values obtained when the magnetic field acts along the three axes  $x, y, z$ , respectively. By an argument similar to that just given, we can show that the average  $C_1$  so defined vanishes. If we denote summation for three perpendicular directions of the magnetic field by  $\sum_{xyz}$  the average is proportional to the term independent of  $H$  in  $(1/H) \sum_{xyz} \sum \partial W^3 / \partial H$  where the second summation extends over all the levels  $W$  in the lowest multiplet level. Using the property of the invariance of the spur, we have

$$\begin{aligned} \frac{1}{H} \sum_{xyz} \sum \frac{\partial W^3}{\partial H} &= \frac{1}{H} \sum_{xyz} \text{Sp} \frac{\partial}{\partial H} (\mathcal{H}_0 + \mathcal{H}' + H\mathcal{H}_1)^3 \\ &= 6 \sum_{xyz} \text{Sp} (\mathcal{H}_0 + \mathcal{H}') \mathcal{H}_1^2 + \dots \\ &= 6 \text{Sp} \left[ (\mathcal{H}_0 + \mathcal{H}') \sum_{xyz} \mathcal{H}_1^2 \right]. \end{aligned}$$

We may replace  $\sum_{xyz} \mathcal{C}_1^2$  by  $(\mu_x^2 + \mu_y^2 + \mu_z^2)(J, M; J, M) = g^2 \beta^2 J(J+1)(2J+1)$  where  $\mu_x, \mu_y, \mu_z$  are the three components of the magnetic moment. Since this is independent of  $M$ , it may be taken outside the Sp sign, so that the mean value of  $C_1$  is proportional to

$$6g^2\beta^2J(J+1)(2J+1)\text{Sp}(\mathcal{C}_0 + \mathcal{C}').$$

Since we have chosen the origin of energy at the mean centre of the unperturbed levels,  $\text{Sp}(\mathcal{C}_0 + \mathcal{C}') = 0$ , and therefore the average value of  $C_1$  vanishes. Since we have shown that the value of  $C$  is independent of the direction of the magnetic field, and since  $\Delta = -C_1/C$ , this may be expressed by saying that  $\Delta$  for a crystal powder vanishes, and hence, neglecting terms of order  $1/T^3$ , the susceptibility obeys the law  $\chi = C/T$ .<sup>8</sup> It must be borne in mind that in deducing this result we have assumed  $kT$  large compared with the splitting produced by the crystal field. However, from our calculations it appears that  $kT$  is of the same order as this splitting at ordinary temperatures. Under these conditions, it is no longer permissible to expand the exponentials as we have done, and on substituting the exact values, deviations from the law  $\chi = C/T$  appear of such a kind that the susceptibility can be represented with considerable accuracy by a formula of the type  $\chi = C/(T + \Delta)$ , where  $\Delta$  is appreciably constant over a wide range of temperature. It is to be hoped that experimenters, after having devoted so much attention to these mysterious  $\Delta$ 's will not be disappointed to find that in a sense they do not exist at all, at least for highly hydrated salts. At very low temperatures there are further deviations, and these will be discussed later.

#### THE POTENTIAL OF THE CRYSTAL FIELD

Each ion is supposed to be subject to an electric field of force represented by a potential  $V$  of the form

$$V = Ax^2 + By^2 + Cz^2 + 0(3) + 0(4) + \dots$$

inasmuch as the first order terms vanish. If the field has cubic symmetry the first nonvanishing terms are of the fourth order; with rhombic symmetry the quadratic terms do not vanish and it is sufficient to consider these alone. The terms of any degree in the expansion of the potential  $V$  must satisfy Laplace's equation. For the quadratic terms this gives  $C = -(A+B)$ . For cubic symmetry, it is sufficient to write the potential

$$V = D(x^4 + y^4 + z^4)$$

since this can be made to satisfy Laplace's equation by adding a function of  $r^2$  (*viz.*  $-3Dr^4$ ). This corresponds to superposing a spherically symmetrical field, and merely shifts all levels equally.

<sup>8</sup> This point was first noticed in a particular case. We are indebted to Professor Van Vleck for the general proof. Sommerfeld, *Atombau und Spektrallinien* I (1931) p. 558, mentions that Bethe has shown in unpublished work that at all but very low temperatures the susceptibility of a crystal powder is the same as that of the free ion.

THE MATRIX ELEMENTS OF THE CRYSTAL FIELD

We require the matrix elements of the squares and fourth powers of  $x$ ,  $y$  and  $z$ , and shall retain only those elements which are diagonal in  $J$ . For a one-electron system they may be calculated by quadrature alone, using the usual form of the hydrogenic wave-function involving  $P_J^M(\cos \theta)$ . For our problem we shall however use the more general method given by Wigner,<sup>9</sup> in which the  $2J+1$  wave functions  $\psi_{JM}$ , of the atom in the state  $J$  are expanded in the form  $\psi_{JM} = \sum_{\lambda} D_{M\lambda}^J(\alpha, \beta, \gamma) \chi_{\lambda}^J(g)$ , where  $\chi_{\lambda}^J(g)$  depends only on the relative positions of the electrons, and  $D_{M\lambda}^J(\alpha, \beta, \gamma)$  is the matrix element of the  $M$ -th row and  $\lambda$ -th column of the  $(2J+1)$ -dimensional representation of the rotation group. The arguments  $(\alpha, \beta, \gamma)$  are Eulerian angles defining the spatial orientation of the atom. The coefficients  $D_{M\lambda}^J$  satisfy certain recurrence relations,<sup>9</sup> by means of which it is possible, though somewhat laborious, to express the quantities  $D_{M\lambda}^J \cos^2 \beta$ ,  $D_{M\lambda}^J \cos^4 \beta$  etc., which occur in the integrands of the required matrix elements, as a linear combination of the quantities  $D_{M\lambda}^J$ . The integration over all orientations  $(\alpha, \beta, \gamma)$  is readily effected by means of the orthogonal relations holding between the coefficients  $D_{M\lambda}^J$  of a representation of the rotation group; the result is to give the matrix elements in the form of a factor involving  $M$ , multiplied by a factor depending on  $J$  and the  $\chi$ 's, with the possible addition of a constant independent of  $M$ . We find for the elements diagonal in  $J$  of the squares and fourth powers of the coordinates of the  $i$ -th electron the following values.

$$z_i^4(M, M) = \gamma - \delta M^2 + \epsilon M^4$$

$$x_i^4(M, M+4) = y_i^4(M, M+4)$$

$$= \epsilon [(J-M)!(J+M+4)!/(J+M)!(J-M-4)!]^{1/2}/16$$

$$z_i^2(MM) = \zeta + \eta M^2, \quad (x_i^4 + y_i^4)(M, M \pm 2) = 0,$$

$$x_i^2(M, M+2) = -y_i^2(M, M+2)$$

$$= \eta [(J-M-1)(J-M)(J+M+1)(J+M+2)]^{1/2}/4.$$

Here  $\gamma, \zeta, \epsilon, \delta, \eta$ , are constants independent of  $M$ ,  $\gamma$  and  $\zeta$  being merely additive. To define the values of  $\epsilon, \delta, \eta$ , we introduce the following abbreviations

$$F = [(J-1)J(J+1)(J+2)(2J-3)(2J-1)(2J+1)(2J+3)(2J+5)]^{-1},$$

$$a = 6J(J-1)(J+1)(J+2), \quad b = -10(6J^2 + 6J - 5),$$

$$c = 70, \quad d = a(2J^2 + 2J - 5),$$

$$e = -(72J^4 + 144J^3 - 132J^2 - 204J + 190),$$

$$f = a(2J-3)(2J+1)(2J+5)/3, \quad g = -3f/J(J+1).$$

<sup>9</sup> E. Wigner, *Zeits. f. Physik* **43**, 624, (1927) and correction in **45**, 601, (1927).

Then in terms of these

$$\begin{aligned}\epsilon &= \sum_{\lambda} \int F(a + b\lambda^2 + c\lambda^4) \chi^2 r_i^4 dg, \\ \delta &= \sum_{\lambda} \int F(d + e\lambda^2 - b\lambda^4) \chi^2 r_i^4 dg, \\ \eta &= \sum_{\lambda} \int F(f + g\lambda^2) \chi^2 r_i^2 dg\end{aligned}$$

where we have written  $\chi^2$  for  $\chi_{\lambda}^J(g)\chi_{\lambda}^{J^*}(g)$  in the integrals. The matrix elements so defined suffice to determine the elements  $\Delta M = 0, \pm 2$  of  $x_i^2 y_i^2 z_i^2$ , and the elements  $\Delta M = 0, \pm 4$  of  $x_i^4 y_i^4 z_i^4$ , which are all that we require, since  $x_i^4$  and  $y_i^4$  occur only in the combination  $x_i^4 + y_i^4$  which has no elements  $\Delta M = \pm 2$ . From these we may pass to the matrix elements of  $\sum_i x_i^2, \sum_i x_i^4$ , etc., occurring in the Hamiltonian, by using relations of the form

$$\sum_i x_i^4(J, M; J' M') = n x_i^4(J, M; J' M')$$

assuming that the  $n$  electrons are all equivalent, which is the case in our problem. In this way we find for the matrix elements of  $\sum_i (x_i^4 + y_i^4 + z_i^4)$

$$\begin{aligned}\sum (x_i^4 + y_i^4 + z_i^4)(J, M; J, M) &= K + pM^2 \{7M^2 + 5 - 6J(J + 1)\} \\ \sum (x_i^4 + y_i^4 + z_i^4)(J, M; J, M \pm 4) &= \frac{1}{2} p [(J \mp M)!(J \pm M + 4)! / (J \pm M)!(J \mp M - 4)!]^{1/2}\end{aligned}\quad (3)$$

where  $K$  and  $p$  are independent of  $M$ .

In order to obtain an idea of the relative magnitude of the constant  $D$  of the crystal field in different cases, it is necessary to examine the constants  $p$  and  $K$  in greater detail. Let us consider a two electron system such as Pr: the analysis can easily be modified for systems with a greater number of electrons. We will assume that  $L (= 5)$  and  $S (= 1)$  are good quantum numbers, these two combining to give the various multiplet levels  $J (= 4, 5, 6)$ . We have

$$x^4 + y^4 + z^4 = \frac{1}{4}(7 \sin^4 \theta - 8 \sin^2 \theta + 4 - \sin^4 \theta \cos 4\phi).$$

The term independent of  $\phi$  gives the matrix elements diagonal in  $M$ , while the term dependent on  $\phi$  gives elements  $\Delta M = \pm 4$ .

Consider the sum  $S$  for one of the permissible  $J$  values

$$S = \sum_M (x^4 + y^4 + z^4)(J, M; J, M) \quad (4)$$

where for brevity we have written  $x^4$  for  $\sum_i x_i^4$  etc. Since all the wave functions for a given  $L$  and  $S$  have the same radial factor, the summation over  $M$  involves averaging (4) over a sphere. The result is clearly

$$\begin{aligned}S &= n(2J + 1) \int_0^{\pi/2} \frac{1}{4}(7 \sin^4 \theta - 8 \sin^2 \theta + 4) \sin \theta d\theta \int_0^{\infty} r^6 R^2(r) dr \\ &= 6I(2J + 1)/5\end{aligned}$$

with  $I = \int_0^\infty r^6 R^2(r) dr$ ,  $n$  being the number of electrons, two in this case and  $R(r)$  the radial wave function of one of the two equivalent electrons. The quantity  $I$  is independent of  $J, L, M, S$  but it does depend on the total quantum number and the effective nuclear charge. For elements so similar in structure as Pr and Nd a good approximation is to assume  $I$  the same for both. A better approximation is to take into account the small difference in the effective nuclear charges. From the relations (3) and (4) it is immediately possible to eliminate the constant  $k$  in the matrix elements and we obtain

$$(x^4 + y^4 + z^4)(J, M; J, M) = 6I/5 + p_J [7M^4 + 5M^2 - 6JM^2(J+1) + 3J(J-1)(J+1)(J+2)/5] \quad (5)$$

the subscript  $J$  on  $p$  being used to denote that  $p$  depends on  $J$ . Transforming from the  $J, M$  system to the  $M_L, M_S$  system, we have from the invariance of the spur in the two representations

$$\sum_J (x^4 + y^4 + z^4)(J, M; J, M) = \sum_{M_L} (x^4 + y^4 + z^4)(M_L, M_S; M_L, M_S), \quad (6)$$

with  $M = M_L + M_S$ , where the matrix elements on the right hand side of this equation can be obtained from (5) by replacing  $p_J$  by  $q$ ,  $M$  by  $M_L$  and  $J$  by  $L$ . The quantity  $q$  depends on  $L$ , but since we are considering only one value of  $L$  there is no need to indicate this dependence.

If we take  $M = 6$ , then  $J = 6$ ,  $M_L = 5$  and  $M_S = 1$ ; Eq. (6) then determines  $p_6$  in terms of  $q$ . By taking in succession  $M = 5$ ,  $M = 4$ , it is possible to find  $p_5$  and  $p_4$  in terms of  $q$ .

It remains now to determine  $q$  in terms of  $I$ . If we transform from the  $(L, S, M_L, M_S)$  system to the  $(m_{l_1}, m_{l_2}, m_{s_1}, m_{s_2})$  system, we have another spur relation,

$$\begin{aligned} & \sum_{LS} (x^4 + y^4 + z^4)(L, S, M_L, M_S; L, S, M_L, M_S) \\ &= \sum_{m_{l_1} m_{l_2}} [(x_1^4 + y_1^4 + z_1^4)(m_{l_1}, m_{s_1}; m_{l_1}, m_{s_1}) + (x_2^4 + y_2^4 + z_2^4)(m_{l_2}, m_{s_2}; m_{l_2}, m_{s_2})] \quad (7) \end{aligned}$$

with  $M_S = m_{s_1} + m_{s_2}$  and  $M_L = m_{l_1} + m_{l_2}$ . There is no need to include  $l_1, s_1$ , etc., since we are going to assume that these are always good quantum numbers. Let us take  $M_S = 1$ ; then we must have  $m_{s_1} = 1/2, m_{s_2} = 1/2$ . Furthermore, if we take  $M_L = 5$ , the only possibility is  $L = 5$ , just the value we require. Moreover, we can evaluate the matrix elements of  $(x^4 + y^4 + z^4)(m_l; m_l)$  for a one-electron problem by quadrature alone. We find

$$\begin{aligned} & (x^4 + y^4 + z^4)(m_l; m_l) \\ &= 3I \frac{7l^4 + 14l^3 - 23l^2 - 30l + 18 - 6l^2 m_l^2 + 5m_l^2 - 6l m_l^2 + 7m_l^4}{2(2l-1)(2l-3)(2l+3)(2l+5)}. \end{aligned}$$

Using this relation and the spur relation (7) one can obtain  $q$  and hence  $p_4$  in terms of  $I$ .



Performing the calculations, we find for Pr

$$p_6 = 14q/33, \quad p_5 = 2q/3, \quad p_4 = 21q/11, \quad q = I/10395 \quad (8)$$

and for Nd

$$p_{15/2} = 33q/91, \quad p_{13/2} = 6q/13, \quad p_{11/2} = 799q/1001, \quad p_{9/2} = 2380q/1001, \quad (9)$$

$$q = I/32670.$$

These relations enable us to find the ratio of the magnitudes of the electric fields in similar salts of these two elements.

#### PRASEODYMIUM

The normal state of Pr is  ${}^3H_4$ ; the multiplet separation between the levels  $J=4$  and  $J=5$  is about  $2100 \text{ cm}^{-1}$ , and hence in calculating the susceptibility the higher multiplet levels may be neglected. This corresponds to discarding off-diagonal elements in  $J$  in the magnetic moment and in the crystal field. Good experimental data have been given by Gorter and de Haas<sup>10</sup> for the variation of the susceptibility of a crystal powder of  $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ .

As has already been explained, the simplest assumption is a cubically symmetrical field. The Hamiltonian is

$$D \sum_i (x_i^4 + y_i^4 + z_i^4) + H\beta\mu_z,$$

$\mu_z$  being the component of magnetic moment along the  $z$ -axis, which is also taken to be the direction of the magnetic field. The diagonal elements arising from the magnetic field are simply  $g\beta HM$ , where  $g$  is the Landé  $g$ -factor ( $=4/5$  for Pr),  $M$  is the component of  $J$  along the axis and  $\beta$  is the Bohr magneton. Bethe<sup>5</sup> has shown that in the absence of a magnetic field the level  $J=4$  splits up into a single level, a doubly degenerate level and two triply degenerate levels. In virtue of the selection rule obeyed by the Hamiltonian, the secular determinant factors into a cubic and three quadratics, two of the quadratics being identical since there is degeneracy as regards the sign of  $M$ . Hence at least one root of the cubic must be identical with one of the roots of the repeated quadratic, while another root must be the same as one of the roots of the remaining quadratic. Thus the determination of the levels in the absence of the magnetic field involves only the solution of quadratic equations. When the magnetic field is present the secular determinant still breaks up into a cubic and three quadratics, the factors being

$$\begin{vmatrix} 4G - 96a - W & s & 0 \\ s & -W & s \\ 0 & s & -4G - 96a - W \end{vmatrix}$$

$$\begin{vmatrix} \pm 3G - 936a - W & t \\ t & \pm G - 216a - W \end{vmatrix} \begin{vmatrix} 2G - 696a - W & 360a \\ 360a & -2G - 696a - W \end{vmatrix}$$

<sup>10</sup> C. J. Gorter and W. J. de Haas, Leiden Comm. 218b.

where

$$s = 24a(70)^{1/2}, \quad t = 120a(7)^{1/2}, \quad G = g\beta H$$

and  $a = pD$ ,  $p$  being the coefficient in the matrix elements (3). Since the roots without the magnetic field are known there is no great difficulty in finding the roots in the presence of the field  $H$  as a power series in  $H$ . For convenience, we choose as origin of energy the centre of gravity of the unperturbed levels. Then the levels in the presence of the field are

$$\begin{aligned} W_1 &= 672a + 5G^2/252a, & W_2 &= 336a + G/2 + 7G^2/3840a, \\ W_3 &= 336a + 2G^2/105a, & W_4 &= 336a - G/2 + 7G^2/3840a, \\ W_5 &= 96a + G^2/180a, & W_6 &= 96a - 180aG^2/, \\ W_7 &= -624a + 5G/2 - 7G^2/3840a, & W_8 &= -624a - G^2/180a, \\ W_9 &= -624a - 5G/2 - 7G^2/3840a. \end{aligned}$$

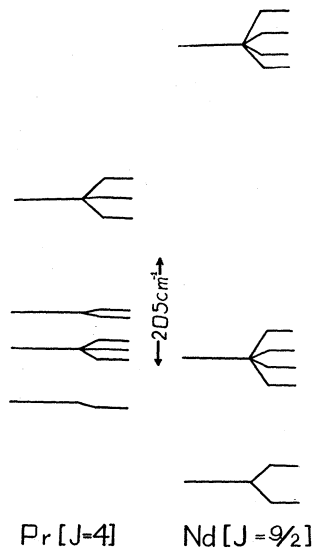


Fig. 1.

The susceptibility per gram atom is then

$$\chi = (2Ng^2\beta^2/a) [53e^{13\mu}/5760 + e^{-2\mu}/30 - 61e^{-7\mu}/2688 - 5e^{-14\mu}/252 + \mu(25e^{13\mu} + e^{-7\mu})/192] \div (3e^{13\mu} + 2e^{-2\mu} + 3e^{-7\mu} + e^{-14\mu}) \quad (10)$$

where  $\mu = 48a/kT$ . The constant  $a$  is chosen so that this formula gives the value of  $\chi_0$ , the susceptibility at the absolute zero of temperature, extrapolated from the experimental data. This gives  $\chi_0 = -10Ng^2\beta^2/a$ , since  $a$  must be negative in order that  $\chi_0$  may be finite. From this we obtain the value  $a = -0.293 \text{ cm}^{-1}$  which corresponds to an over-all splitting produced by the crystal field of  $389 \text{ cm}^{-1}$ . Fig. 1 gives the way in which the crystal field splits the lowest multiplet level of Pr. The same figure gives similar results for Nd, and the influence of the magnetic field in removing the degeneracy is also shown. The curve  $1/\chi$  against  $T$  is given in Fig. 2 and on it are marked the ex-

perimental values for  $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  as measured by Gorter and de Haas.<sup>10</sup> The agreement is extremely good. In order to show the sensitivity to variations in  $a$  we have plotted the curves (1)  $a = -0.37 \text{ cm}^{-1}$  (2)  $a = -0.293 \text{ cm}^{-1}$  (3)  $a = -0.30 \text{ cm}^{-1}$ , while the straight line (4) through the origin gives the asymptote for all values of  $a$  at very high temperatures (but not high enough for the higher multiplet levels to count). This straight line represents the Hund formula for the susceptibility  $\chi = N\beta^2 g^2 J(J+1)/3kT$ , obtained on the assumption that the ion is perfectly free. It should be explained that the experimental values are given per gram ion. The molecular weight of  $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  is 714, and since there are two Pr atoms it is necessary to divide  $\chi$  as given by Eq. (10) by 357 in order to give the  $\chi$  used by experimenters and employed in Fig. 2. In the temperature range 100°K to 300°K the experimental

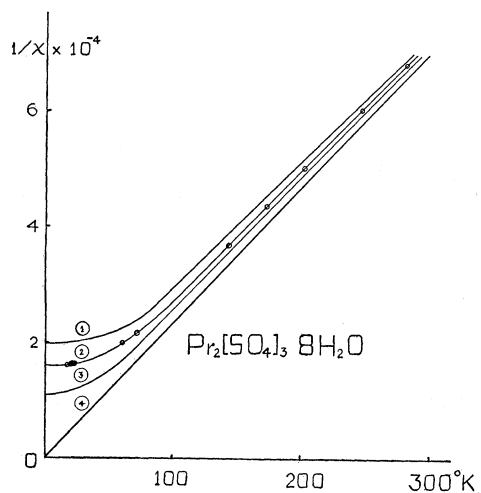


Fig. 2.

$\Delta$  is 32°, while the theoretical value is about 25°. The difference is too small to show in the figure. More will be said about the agreement with experiment when we have considered Nd.

Before it was realized that a field of cubic symmetry would give such a good account of the experimental results, a field of rhombic symmetry was tried, but with little success. A simple assumption in this case is that the potential of the field is of the form  $A(x^2 + y^2 - 2z^2)$ . Since the measurements were made on crystal powders, it is necessary to average over all directions. This can be accomplished by first solving the problem where the magnetic field acts along the  $z$ -axis, the axis of symmetry, and then when it acts perpendicularly to the axis. The average susceptibility will be the average of these two, taken with the weights one and two respectively. The problem bears a formal resemblance to the problem of the symmetrical top; the group  $J=4$  of energy levels are all doubly degenerate except one which is single and which must be taken as the lowest in order to fit the observed susceptibility at low temperatures. However the temperature dependence of the susceptibility calculated

on the assumption of a "symmetrical top" field bore very little resemblance to that observed and it was necessary to reject it. If data were available on single crystals one could tell immediately by comparing the three principal susceptibilities and  $\Delta$ 's how good an assumption a field of cubic symmetry is. If the three are equal, everything would be very satisfactory; if not, then one would have to introduce a small field of rhombic symmetry to account for the differences. The effect of introducing a field of rhombic symmetry would be to give three principal Curie constants and three principal  $\Delta$ 's, and the  $\Delta$ 's would not vanish even at high temperatures although the Curie constants would then all become equal and the mean  $\Delta$  would vanish. Nothing further can be said until experiments have been made on single crystals.

NEODYMIUM

The normal state of Nd is  ${}^4K_{9/2}$  ( $K$  states have  $L=6$ ). The multiplet separation between  $J=9/2$  and  $J=11/2$  is about  $1800\text{ cm}^{-1}$  and at room temperatures one ought not to neglect the higher multiplet levels. We are indebted to Miss Frank for the information that the correction for the other multiplet levels is to add about three percent to the susceptibility at room temperatures.<sup>11</sup> However we make no attempt to apply this correction, since the discrepancy between different observers is considerably greater than this. Since the ground state has  $J=9/2$ , so that  $J$  is a half integer, the electric field, as shown by Kramers,<sup>12</sup> will be unable to remove all the spatial degeneracy of this state; each level will be at least doubly degenerate and will have a Zeeman effect of the first as well as of the second and higher orders. It is known from the work of Bethe<sup>5</sup> that in the absence of the magnetic field the ten components of  $J=9/2$  fall into two coincident groups of five on account of the Kramers two-fold degeneracy, and each group of five levels will split up into a single level and two doubly degenerate levels. In the presence of the magnetic field, the factoring is into a quadratic and a cubic, given by

$$\begin{vmatrix} 9G/2 + 5Av - W & 6A & 0 \\ 6A & G/2 + 5Av - W & 10A \\ 0 & 10A & -7G/2 - 3Av - W \end{vmatrix} \begin{vmatrix} 5G/2 + 2Av - W & 5Au \\ 5Au & -3G/2 - 2Av - W \end{vmatrix}$$

<sup>11</sup> Miss Frank has shown, *Phys. Rev.* **39**, 119 (1932), that it is very important to take into account the off-diagonal elements in  $J$  in the magnetic moments for Eu and Sm, since for these the separation between the two lowest multiplet levels is not small compared with  $kT$ . For Eu, the lowest level has  $J=0$ , the next lowest  $J=1$  and neither of these breaks up under the action of a crystal field of cubic symmetry nor is their relative position altered to a first approximation; and since they belong to different representations of the cubic group, the field does not introduce elements of magnetic moment between them. From analogy with the conclusions given in the present paper, one would expect the crystal fields in the rare earths to have cubic symmetry. If this is so, Miss Frank's calculations for Eu still apply. For Sm, whose two lowest levels have  $J=5/2$  and  $J=7/2$  as normal states, it may be necessary to amend the results given in her paper. Further calculations will be made on this point.

<sup>12</sup> H. A. Kramers, *Proc. Amst. Acad.* **33**, 959 (1930).

where  $u = (6)^{1/2}$ ,  $v = (14)^{1/2}$ ,  $G = g\beta H$  ( $g = 8/11$  for Nd) and  $A = 12ap(14)^{1/2}$ . The origin of energy has been chosen to make the spur of the quadratic zero, a device which greatly simplifies the algebra. The cubic and quadratic arising from the other quintic can be obtained from those above by changing the sign of  $G$ . The roots in the absence of the magnetic field can readily be obtained, since then the roots of the quadratic must also be roots of the cubic. Solving these equations up to terms in  $H^2$ , we find for the ten energy levels

$$\begin{aligned} W_1 &= 20.95A + 1.833G + 0.3879G^2/A, & W_2 &= 9.11A + 2.788G - 0.3411G^2/A, \\ W_3 &= 9.11A - 0.542G + 0.1015G^2/A, & W_4 &= -19.59A - 3.121G - .00468G^2/A \\ W_5 &= -19.59A + 1.542G - 0.1015G^2/A. \end{aligned}$$

and five more obtained from these by changing the sign of  $G$ .

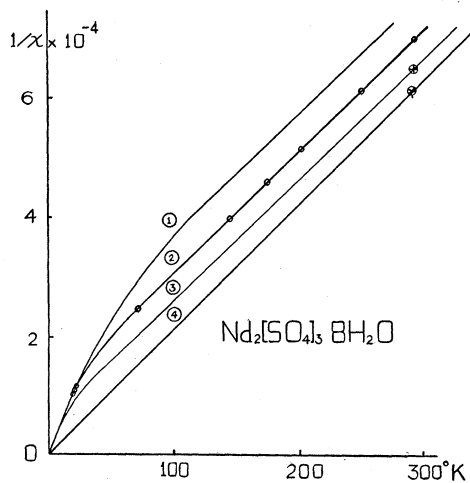


Fig. 3.

The expression for the susceptibility per gram atom is

$$\begin{aligned} \chi &= (2g^2\beta^2N/A) [(0.1483e^{19.59\mu} + 0.2396e^{-9.11\mu} - 0.3879e^{-20.95\mu}) \\ &+ \mu(6.065e^{19.59\mu} + 4.031e^{-9.11\mu} + 1.680e^{-20.95\mu})] \\ &\div [2e^{19.59\mu} + 2e^{-9.11\mu} + e^{-20.95\mu}], \end{aligned}$$

where  $\mu = A/kT$ . To obtain the susceptibility per gram ion it is necessary to divide by 361. As with Pr,  $a$  is negative, and its value is about  $-0.458 \text{ cm}^{-1}$  ( $A = -20.6 \text{ cm}^{-1}$ ), which gives an over-all splitting of  $834 \text{ cm}^{-1}$ . The splitting of the lowest multiplet level produced by the crystal field is shown in Fig. 1. Curve 2 in Fig. 3 gives the theoretical variation of  $1/\chi$  with  $T$ , while on it are marked the experimental results of Gorter and de Haas.<sup>10</sup> The agreement is extremely good. Curves 1 and 2 in Fig. 3 show the sensitivity to  $A$  and are for the values  $A = -36 \text{ cm}^{-1}$  and  $A = -12 \text{ cm}^{-1}$  respectively, while the straight line 4 gives as before Hund's law. The measurements of Cabrera<sup>13</sup> at  $290^\circ\text{K}$ ,

<sup>13</sup> B. Cabrera, C. R. 180, 669 (1925).

and of Zernicke and James<sup>14</sup> at 293°K, and of St. Meyer,<sup>15</sup> which agree almost exactly with Zernicke and James, are also marked and are seen to fall considerably below those of Gorter and de Haas. If, on account of some error in calibration, it should prove necessary to reduce the experimental values by a constant factor,  $D$  can still be chosen to fit the results. Exactly the same discrepancies appear with Pr. Again, the susceptibility as measured by Cabrera is 11 percent higher, and that measured by Zernicke and James and also by St. Meyer is 2 percent higher, than that obtained by Gorter and de Haas, all at room temperature. The disagreement in this case is not quite so bad as with Nd.

Using the relations (8) and (9) we can compare immediately the values of the constants  $D$  of the crystal fields in the two salts  $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  and  $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , on the assumption that the integral  $I$  is the same in both cases. This is not quite accurate and rather favors Pr, but it is sufficiently close for our purpose. The constant  $D$  for Nd is found to be about 3.9 times that for Pr. One would expect the electric fields in two salts so similar in every way to be of about the same magnitude. It should be remembered, however, that we determine this magnitude from the difference between the observed magneton number and the Hund value, and a small change in the observed magneton number will make a considerable difference in the calculated field. For example, the difference between the magneton number of Nd as measured by Cabrera, and the Hund value, is 0.08, while Gorter and de Haas obtain 1.24. For Pr the corresponding figures are 0.17 and 0.76 respectively. The electric fields calculated from Cabrera's values are much less than those given here. More accurate data on the susceptibilities, even at one temperature, would allow this question to be settled satisfactorily.

In conclusion we desire to express our sincere thanks to Professor J. H. Van Vleck, whose advice and criticism during the course of this work have been invaluable.

<sup>14</sup> J. Zernicke and C. James, *Jour. Am. Chem. Soc.* **48**, 2827 (1926).

<sup>15</sup> Stefan Meyer, *Phys. Zeits.* **26**, 51, 478 (1925).