On the Paramagnetic Rotation of Tysonite

J. H. VAN VLECK AND M. H. HEBB, *University of Wisconsin*

(Received May 12, 1934)

It is shown both theoretically and by examination of the Leiden experimental data on CeF_3 and tysonite that in rare earth compounds the Verdet constant V should exhibit the same dependence upon temperature as does the magnetic susceptibility χ, even when Curie's law is not obeyed. In consequence of the similarity in the mode of variation with temperature for V and χ, existing data on the temperature variation of χ can be considerably enhanced by drawing upon the Faraday measurements of Becquerel and de Haas. In particular, information concerning the χ's for individual crystallographic axes thus becomes available in tysonite and the tests of calculations of the susceptibility with crystalline potentials become correspondingly severe. The triclinic field proposed by Kramers for tysonite does not appear to account for the behavior of individual principal susceptibilities, although adequate for the mean characteristic of a crystal powder. It is shown that somewhat better agreement with experiment can be achieved by assuming tentatively that the local field has rhombic symmetry, with three possible orientations for the rhombic axes differing from each other by 120°, so that all told the crystal has the desired hexagonal symmetry. Such staggered rhombic fields are compatible with Oftedal's x-ray analysis of the crystallographic structure of tysonite, except that the deviations of the fields from axial character seem rather large.

INTRODUCTION

THE well-known measurements on the Faraday effect of paramagnetic salts at low temperatures, made at Leiden by Becquerel and de Haas,[1] are valuable as an alternative means of determining effective magneton numbers and other magnetic properties usually found from experiments on suceptibilities. Hitherto only the saturation properties of the magnetic rotation appear to have been generally[2] correlated with susceptibility. It is the purpose of the present paper to show, both by theory and by calculation from experimental data that, under certain conditions, the temperature variation of the Verdet constant V (rotation per unit length, divided by field strength) is, apart from an additive constant, the same as that of the magnetic susceptibility χ. Then

$$V=A\chi+K, \tag{1}$$

where K is a constant independent of temperature. Becquerel and Kramers confined[3] their analysis to temperatures so low that they could take $K=0$, and appear to have always regarded A as an undetermined function of the temperature, so that they could only utilize relations of the form

$$V(H_2, T_1)/V(H_1, T_1)=\chi(H_2, T_1)/\chi(H_1, T_1), \tag{2}$$

whereas we propose to show that it is often allowable to take

$$\frac{V(H_2, T_2)-K}{V(H_1, T_1)-K}=\frac{\chi(H_2, T_2)}{\chi(H_1, T_1)}. \tag{3}$$

Here H_1, H_2 denote two arbitrary field strengths, and T_1, T_2 two temperatures. As compared with (2), Eq. (3) greatly enhances the utility of the Faraday data, for (2) is of no value unless the field H is so great and the temperature so low as to permit observation of the saturation effect $\chi(H, T_1)\neq\chi(O, T_1)$.

---

[1] Jean Becquerel and W. J. de Haas, Proc. Amsterdam Acad. **32**, 523 (1929); J. Becquerel and W. J. de Haas, ibid. **32**, 536, 578, 590, 733, 874, 913, 926, 937 (1929–30); or Leiden Communications, Nos. 191, 193, 199, 211.

[2] It was mentioned long ago by Becquerel, and somewhat later independently by Ladenburg, that V and χ are both often linear in $1/T$, in which case Eq. (1) is obviously valid. Our emphasis, however, is on the applicability of (1) in the general case that Curie's law is not obeyed and it is primarily in this non-linear case that we find (1) particularly useful.

[3] H. A. Kramers, Proc. Amsterdam Acad. **32**, 1176, **33**, 959 (1929–30); H. A. Kramers and J. Becquerel, ibid. **32**, 1190 (1929); or Leiden Communications 204 and supplement 68.

1. Theory for Rare Earth Ions

The Verdet constant V for light of frequency ν is given by the expression[4]

$$V=(4\pi^2\nu^2B/Hch)\Sigma_{mn'j'm'}\tau(n'j'm';\,njm)[P_x(n'j'm')P_y]_{mm}e^{-W_{njm}/kT},\tag{4}$$

where

$$B=N/\Sigma_m e^{-W_{njm}/kT},\qquad \tau(n'j'm';\,njm)=1/[\nu^2-\nu(n'j'm';\,njm)^2].\tag{5}$$

The matrix elements of the x component of electric moment are denoted by $P_x(n'j'm';\,njm)$ etc. To avoid excessive explicit printing of these elements, we find it convenient to introduce the abbreviation

$$[P_x(n'j'm')P_y]_{mm''}=i[P_x(njm;\,n'j'm')P_y(n'j'm';\,njm'')-P_y(njm;\,n'j'm')P_x(n'j'm';\,njm'')].\tag{6}$$

The direction of the magnetic field H we take to be the z axis. The indices j and m denote respectively the inner and magnetic quantum numbers, while n signifies all quantum numbers other than j, m. The effect of n and j on the energy W is supposed large compared to kT. This supposition is warranted for all the rare earths except Sm, Eu, to which elements Eqs. (1) and (3) are consequently not applicable. It permits us to neglect, as is usual, the part of the Zeeman effect arising from elements non-diagonal in j.

If we disregard modulation of frequencies by the magnetic field we may set

$$\nu(njm;\,nj'm')=\nu(nj;\,n'j'),\qquad \tau(n'j'm';\,njm)=\tau(n'j';\,nj).\tag{7}$$

Actually this modulation is not negligible and gives rise to well-known, so-called "diamagnetic" terms, which have been calculated by Kuhn, Rosenfeld[5] and others. As long as H is the only external field, these terms are independent of T and unimportant at low temperatures. The Kronig-Hönl formulas for Zeeman components yield relations of the form[6]

$$[P_x(n'j'm')P_y]_{mm''}=m\delta_m^{m''}C_{nj},\tag{8}$$

where C_{nj} depends on n, j but not on m.

The paramagnetic susceptibility is

$$\chi=(Bg\beta/H)\Sigma_m me^{-W_{njm}/kT},\tag{9}$$

with the understanding that W_{njm} is inclusive of Zeeman energy. Here g is Landé's factor, and β is the Bohr magneton $he/4\pi mc$. If we substitute (7) and (8) in (4), then the terms in (4) corresponding to every value of n, j have the same dependence on T and H as does (9), except for a constant proportional factor and consequently (1) is proved, with so far $K=0$. (The dependence on H is mainly implicit, through W_{njm}.)

Introduction of a Crystalline Field. The preceding argument is essentially the same as Rosenfelds', but now we must go further, and insert a crystalline field, of the type treated by Bethe,[7] Kramers,[3] Penney,[8] Schlapp[8] and Van Vleck.[9] This complication is necessary for it is precisely what makes the temperature variation complex and interesting. The Hamiltonian function will cease to be diagonal in the original, equatorial system of representation. Instead, to diagonalize the crystalline plus Zeeman energy, one must make a canonical transformation to a new system, symbolized by indices j^*, m^*. We shall assume that the crystalline potential may be considered diagonal in n. This is doubtless a good approximation, for any perturbations due to non-diagonal elements in n are of the unimportant, high-frequency type. We shall also assume that in the ground state the non-diagonal elements of this potential in j can be disregarded, as here the Stark effect is smaller and the spin

---

[4] H. A. Kramers, Proc. Amsterdam Acad. **33**, 959 (1930); R. Serber, Phys. Rev. **41**, 489 (1932).

[5] W. Kuhn, Math. Phys. Comm. Dan. Acad. vii, **12**, 11 (1926); L. Rosenfeld, Zeits. f. Physik **57**, 835 (1930).

[6] Cf. L. Rosenfeld, Zeits. f. Physik **57**, 838–839 (1930).

[7] H. Bethe, Ann. der Physik **3**, 133 (1929).

[8] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932); R. Schlapp and W. G. Penney, ibid. **42**, 666 (1932).

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

multiplets wider than for the excited states. The new index m^* may, in a certain sense, still be regarded as a spatial quantum number but it ceases to have the usual axial significance of quantizing a component of angular momentum. For example, m^* will be nearly a "cubic" rather than equatorial quantum number if the external field is of cubic symmetry except for the magnetic portion H. Under our hypotheses, the transformation matrix from the old to new system is of the form

$$S(n'jm;\, n^*j^*m^*)=\delta_{n'}{}^{n^*}S_{n'}(jm;\, j^*m^*), \qquad S(njm;\, n^*j^*m^*)=\delta_{nj}{}^{n^*j^*}S(m;\, m^*), \tag{10}$$

and the susceptibility is

$$\chi=(Bg\beta/H)\Sigma_{m,\, m^*}\, m\,|S(m;\, m^*)|^2e^{-W_{njm^*}/kT}, \tag{11}$$

with, of course, the understanding that now the letter m^* rather than m is to be used in connection with the definition of B. The Verdet constant is still given by (4) except that m^*, $j^{*\prime}$, $m^{*\prime}$ everywhere replace m, j', m'. If it is allowable to neglect the effect of m^*, $j^{*\prime}$, $m^{*\prime}$ on the frequency, and thus set

$$\tau(n'j^{*\prime}m^{*\prime};\, njm^*)=\tau(n'j';\, nj), \tag{12}$$

then one can take τ outside the summations over m^*, $j^{*\prime}$, $m^{*\prime}$. When this simplification is possible, use can be made of the relation

$$\Sigma_{j^{*\prime},\, m^{*\prime}}[P_x(n'j^{*\prime}m^{*\prime})P_y]_{m^*m^*}=\Sigma_{j',\, m'}[P_x(n'j'm')P_y]_{mm}\,|S(m;\, m^*)|^2, \tag{13}$$

which is essentially a special case of the principle of spectroscopic stability and is readily established from the orthogonality properties of the transformation (10) and the occurrence of the Kronecker δ factor in (8). In virtue of (12), (13) and (8), the new version of (4) becomes

$$V=(4\pi^2\nu^2B/Hch)\Sigma_{n'j'}\{C_{n'j'}\tau(n'j';\, nj)\ \Sigma_{m,\, m^*}m\,|S(m;\, m^*)|^2e^{-W_{njm^*}/kT}. \tag{14}$$

Eq. (14) differs from (11) only by factors independent of H, T, and so (1) retains its validity, with $K=0$ as yet. The K term should, however, be added to allow for the well-known diamagnetic rotation which arises from the modulation of the frequency factors, and also sometimes of the amplitude factors, by the magnetic field. Besides diamagnetic contributions, the K term may be regarded as including also the effect of the matrix elements of the magnetic moment which are non-diagonal in j. This term is really independent of temperature only as long as the effect of the crystalline potential is negligible, i.e., as long as this potential is small compared with kT. At low temperatures this condition will not be fulfilled but then the paramagnetic rotation far overshadows the diamagnetic. Hence, little harm is done if K is treated as independent of temperature.

The crux of the whole matter is whether (12) is a legitimate approximation. Naturally (12) is a much more severe restriction than (7), for the dependence of ν on m^* is due to crystalline Stark as well as Zeeman effect and is so much larger than the purely Zeeman dependence discarded in assuming (7). We shall consider specifically the case of Ce^{+++}. Here most of the rotation appears to be due to a band at 2500A, which, as first noted by Freed,[10] is doubtless to be attributed to the transition $4f-5d$. The Stark effect for the ground level $4f$ cannot amount to over 1000 cm^{-1} or so, as otherwise the susceptibility would not conform as well as it does to Hund's formula.

---

[10] S. Freed, Phys. Rev. **38**, 2122 (1931); It has often been suggested by spectroscopists that the ground state of Ce^{+++} is perhaps a $5d$ rather than $4f$ state. Such an alternative, however, seems entirely incompatible with the conformity of the susceptibility of cerium salts to Hund's formula at high temperatures. The spectroscopic evidence favoring $5d$ is an extrapolation from the spectrum of Cs I and Ba II (cf. Gibbs and White, Phys. Rev. **33**, 157, 1929). Such an extrapolation, however, is not really applicable, because the $4f$ orbit is of a different nature in Ce than in Ba, as in Ce^{+++} it is situated in the interior rather than exterior of the atom. In other words an extrapolation cannot be used to compare states located in different potential valleys. The theoretical calculations of Wu (Phys. Rev. **44**, 727 (1933) are not open to this objection, and still place $5d$ below $4f$ but the potential field utilized by Wu may not be accurate enough to make this conclusion reliable. On the other hand, very recently Roberts, Wallace and Pierce (Phil. Mag. **17**, 934, 1934) have found that the magnetic rotary dispension of aqueous solution of $Ce_2(SO_4)_3$ favors a $4f$ rather than $5d$ ground level for the Ce^{+++} ion.

The Stark splitting for the $5d$ level can be somewhat greater, as this is an excited state. Unfortunately the series limit for the spectroscopic terms of Ce^{+++} is unknown but this may be approximately located from the known[11] separation of the $5d$ and $6d$ terms if we assume that these terms conform approximately to the Rydberg formula $16R/(n+\Delta)^2$. This gives $\Delta=-2.1$ for d terms, making $5d=215{,}000\ \mathrm{cm}^{-1}$ and hence $4f=255{,}000\ \mathrm{cm}^{-1}$. Thus there is little relative difference between the firmness of binding of the $4f$ and $5d$ orbits. The Stark splitting should be somewhat greater, though, for a $5d$ than for a $4f$ orbit of equal firmness, due to the greater eccentricity of $5d$. It seems plausible that the crystalline Stark effect for $5d$ does not greatly exceed $10^3\ \mathrm{cm}^{-1}$ in magnitude. Since $4f-5d$ is about $40{,}000\ \mathrm{cm}^{-1}$, it is seen that (12) is approximately true if this is the case. Strong experimental evidence that the Stark effect for $5d$ is not excessive is furnished by the mere existence of absorption bands for Ce^{+++} at approximately 2500A in a variety of compounds. Freed, for instance, finds that the position of the band does not differ by more than 100A or so, for the ethyl sulphate and for the hydrated chloride of cerium.

The absorption observed by Freed for Ce^{+++} near 2500A is diffuse rather than discrete in structure. As he mentions, this is probably because of the complicated modulations of the $5d$ state due to interaction with the inter-atomic vibrations in the crystal. Such interaction is, of course, not covered by the Bethe-Kramers method of static crystalline potentials. The amplitudes of the inter-atomic vibrations, of course, vary with temperature and this will mean that the absorption frequencies ν are to a certain extent a function of the temperature. It is partly for this cause that Kramers regards the proportionality factor A in (1) as an undetermined function of the temperature. However, we believe that any variation of A due to this cause is a relatively unimportant factor, particularly below room temperatures. This, for one thing, is indicated by the fact that Freed finds no great shift of absorption frequency with temperature. He finds that the absorption near 2500A can usually be divided into three component bands, occurring at roughly 2575, 2450, and 2300A. Possibly the three components are to be correlated with different Stark and spin components of the $5d$ state, each component being diffuse because of spread due to vibrational modulation. If so, the Stark splitting of $5d$ is of about the order estimated in the preceding paragraph.

Besides the above rotation due to $4f-5d$, we must also in Ce^{+++} consider that due to $4f-5g$. (The higher members $4f-md$, $m=6, 7, \cdots$ and $4f-mg$, $m=6, 7, \cdots$ are definitely less important, as the higher d members have much smaller τ factors than that for the first member $5d$, while the higher g members have much smaller amplitudes than for $5g$.) The $5g$ state is probably closely hydrogenic and then $4f-5g$ is about $185{,}000\ \mathrm{cm}^{-1}$. The Stark effect for $5g$ is undoubtedly much larger than for $5d$, perhaps of the order $10^4\ \mathrm{cm}^{-1}$. Even with this estimate, however, Eq. (12) is still approximately valid as applied to the transition to $5g$, thanks to the large value of the frequency $4f-5g$. The sign of the observed Faraday effect in solutions containing cerium shows quite definitely that $4f-5d$ is a much more potent line for the Faraday effect than $4f-5g$.[12] This fact presents an interesting theoretical problem. The magnitude of $\tau(4f;\,5d)$ is, to be sure, much greater than that of $\tau(4f;\,5g)$. The ratio of the two τ's is, for instance, about 30 if the incident light has a wave-length of 5000A. However, the amplitude $a(4f;\,5g)$ is much greater than $a(4f;\,5d)$, in fact over ten times greater if one makes a calculation with hydrogenic wave functions.[13] This is because the bulk of the $4f-g$ absorption intensity is concentrated in the first line $4f-5g$, whereas $4f-5d$ consumes only a small part of the $4f-d$ absorption. The departures from hydrogenic conditions must thus be such as to make $a(4f;\,5d)^2/a(4f;\,5g)^2>1/30$ rather than $<1/100$. That such departures may be large is clear from the fact that the $4f$ orbits in the rare earths occupy inner rather than peripheral regions of the atom. In Ce^{+++}, in particular, the $4f$ state has an effective quantum number $n^*=2.6$ and so is bound over twice as firmly as one would calculate for a hydrogen-like atom with $Z=4$. That actually the amplitude for $4f-5d$ is more important relative to other amplitudes emanating from $4f$ than in a hydrogen-like atom is shown by the following consideration. The squares of the amplitudes emanating from a given state sum to the mean square radius of this state. Since $r\sim n^{*2}$ the mean square radius for $4f$ differs from the hydrogenic value by a factor roughly $(2.6/4)^4=0.2$. On the other hand, Gorter's[12] measurements on the absolute amount of Faraday rotation indicate that the amplitude for $4f-5d$ has approximately the hydrogenic value. Hence the relative importance of this amplitude is increased by

---

[11] J. S. Badami, Proc. Phys. Soc. London **43**, 53 (1931).

[12] C. J. Gorter, Phys. Zeits. **34**, 238 (1933); Roberts, Wallace and Pierce, reference 10.

[13] Cf. calculations of hydrogenic amplitudes by Slack, reported by L. R. Maxwell, Phys. Rev. **38** 1685 (1931).

a factor $5^{\frac{1}{2}}$. On the other hand, a corresponding increase for $4f-5g$ is impossible and this amplitude must be about $5^{-\frac{1}{2}}$ the hydrogenic value, since otherwise the squares of the amplitudes for $4f-g$, already due almost entirely to $4f-5g$, would sum to more than the mean value of r^2 for $4f$.

Salts of the iron group are not in general amenable to any of the preceding theory, as here the crystalline potential is large compared to the spin-orbit energy, and produces a large electric Paschen-Back effect on the ground state. J. H. Van Vleck and W. G. Penney[14] will show elsewhere that a possible exception is furnished by manganous and ferric compounds for which the crystalline fields have cubic symmetry. In such ions the ground state is ^5S and the important absorption lines are $^5S-{}^5P$. Cubic fields do not decompose either S or P states, except for spin-orbit complications. Thus in cubic ferric or manganous crystals, V and χ are possibly sometimes proportional.

2. Experimental Confirmation in Tysonite

Tysonite is the rare earth mineral for which the most comprehensive rotational data are available at present. It is a mixed crystal (La, Ce, Nd+Pr, F_3). Cerium is known to be responsible for most of the rotation, probably because of the comparatively low value of the frequency $4f-5d$ in Ce^{+++} (cf. section 1). To make a proper test of (1), one must compare the Verdet constant of tysonite with the susceptibility of CeF_3 rather than of tysonite, since the susceptibility of tysonite arises only partially from Ce. The x-ray measurements of Oftedal[15] reveal that tysonite and CeF_3 are similar in crystal structure and dimensions, except, of course, for the variable cation (La, Ce, Nd, Pr) in the former. Hence the crystalline fields surrounding Ce^{+++} are nearly similar in the two materials.

The suceptibility of CeF_3 crystal powder has been measured by de Haas and Gorter.[16] The Verdet constant $V_\perp$ perpendicular to the crystal (i.e., optic) axis has been determined recently by Becquerel,[1] while that parallel to this axis has been available for some time. Since tysonite has hexagonal symmetry, the Verdet constant should have the same value for all directions orthogonal to the crystal axis, except for saturation effects which will be deferred until sections 3 and 6. For weak fields, the mean Verdet constant analogous to that for a powder equals $(V_{||}+2V_\perp)/3$. The comparison of susceptibility with rotation is given in Table I, along with the underlying experimental data.[17] The constancy of the ratio in the next to last column is a test of Eq. (1) with $K=0$. The deviation at the highest temperature might be expected, since here the diamagnetic correction K will be most important. In the last column, the Verdet constant is modified by subtraction of a term $K=0.67\times10^{-3}$ independent of T. This value of K has been so determined as to make the ratio in the last column have the same value at 20.4°K as at 293°K.

TABLE I. *Comparison of susceptibility with rotation.*

Temperature	Tysonite $V_{\|\|}\times10^3$	Tysonite $V_\perp\times10^3$	CeF_3 $\chi\times10^6$	$\left[\frac{\chi\times10^3}{\frac{1}{3}(V_{\|\|}+2V_\perp)}\right]$	$\left[\frac{\chi\times10^3}{\frac{1}{3}(V_{\|\|}+2V_\perp)-.67\times10^{-3}}\right]$
293°K	−6.17	−5.11	11.2	−2.05	−1.83
77.5°	−22.17	−12.84	29.3	−1.84	−1.76
20.4°	−73.3	−24.4	75.8	−1.86	−1.83
14.4°	−101.9	−30.3	100.8	−1.86	−1.84

The slight variation of the entries in either of the last two columns is gratifying when it is remembered that the experimental determination of $V_\perp$ is exceedingly difficult and that tysonite and CeF_3 are, after all, not exactly identical crystals. The approximate validity of (1) enables us to translate measurements of Verdet constants

---

[14] J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).

[15] I. Oftedal, Zeits. f. physik. Chemie **B5**, 272 (1929); **13**, 190 (1931).

[16] W. J. de Haas and C. J. Gorter, Proc. Amst. Acad. Sci. **33**, 349 (1930) (or Leiden Communication 210c).

[17] Just as the present paper was completed, an article appeared by J. Becquerel, W. J. de Haas and J. van den Handel, Physica **1**, 383 (1934), giving a value of $V_{||}$ at 293°K 4.6% higher than that shown in Table I. This reduces $-(\chi/V)10^3$ from 2.05 to 2.01. Unfortunately, new measurements on the perpendicular component are not available but if they should increase $V_\perp$ in the same ratio, the value of $-(\chi/V)10^3$ at 293° would be lowered from 2.05 to 1.96. The corresponding change at 77°K is only slight, *viz.*, from 1.84 to 1.82. At temperatures below 20°K we have always utilized the new measurements on the parallel component, as these were communicated to us by Professor Becquerel in advance of publication. We wish to take this opportunity of expressing our indebtedness to Professor Becquerel for this material. Use of the new data does not affect our points on Fig. 2 at 293° if we assume that Becquerel's old value for the anisotropy $V_\perp/V_{||}$ is still correct.

into determinations of magnetic susceptibility and so greatly enriches our magnetic data, since the V of tysonite, unlike the χ of CeF_3, has been determined for individual crystallographic axes.

It is probably better to take the diamagnetic correction K to be negligible, i.e., of order 10^{-5}, rather than to be 0.67×10^{-3}, for the following reasons. First, in cerium ethyl sulphate, which should presumably be comparable with tysonite as regards the rough order of magnitude of K, Becquerel and de Haas[18] have presented fairly convincing evidence that K is only 3×10^{-5}. Second, it is hard to understand how χ/V could be lower at 77°K than at 20° and 293°, as would be required if $K=0.67\times10^{-3}$. On the other hand, the anomaly in χ/V at room temperatures which is concomitant to taking $K=0$ might be blamed on a shift of absorption centers with temperature or something of the kind. Hence in the following work we shall not use the value of V at 293° except that we shall make the reasonable assumption that the anisotropy in χ at 293°K is the same as that in V. This is necessary in order to have data available on individual axes at room temperatures and is tantamount to raising the values of V at 293° in the ratio 2.05/1.86. If, instead, one preferred to take $K=0.67\times10^{-3}$, the only material change would be to raise the values of n_B slightly at 77°K as shown by the solid circles in Fig. 2.

3. EVIDENCE FOR A DEMAGNETIZING MOLECULAR FIELD IN TYSONITE

Unless the crystalline field has unusual symmetry, the Boltzmann factor is negligible at low temperatures for all but one pair of levels in an ion with an odd number of electrons such as Ce^{+++}. Such a pair we shall call a Kramers doublet. Because of Kramers' theorem,[19] the components of a doublet separate only in virtue of the magnetic field and have Zeeman energies $W_0\pm\mu\beta H\ (+H^2)$. The susceptibility is given by the expression

$$\chi=I/H=(N\mu\beta/H)\tanh\left[\mu\beta(H-\gamma I')/kT\right]+2N\left(\frac{H-\gamma I'}{H}\right)\sum_{n'(n'\neq n)}\frac{|m_H(n;n')|^2}{h\nu(n';n)},\qquad(15)$$

where the matrix elements of the magnetic moment in the direction of the field H are denoted by $m_H(n;n')$ and n' always refers to other doublets than the basic pair n. The term involving the hyperbolic tangent originates with Kramers and Becquerel[3] and is inclusive of the correction for saturation. On the other hand, we always neglect saturation in writing the second term, which represents the contribution of the high frequency elements. This is allowable, for surely βH is small compared with the crystalline Stark separation.

In writing Eq. (15) we have taken the argument of the hyperbolic tangent to be $\mu\beta(H-\gamma I')/kT$ rather than $\mu\beta H/kT$, in order to allow for the exchange effects which couple together the spins of the various paramagnetic ions. It is a well-known result of Heisenberg's theory of magnetism that these effects are approximately equivalent to superposition of a Weiss molecular field $-\gamma I'$ upon the applied field H, so that the total effective field is $H-\gamma I'$, where I' is the intensity of magnetization. The prime is affixed to I to indicate that it refers to the entire mixed crystal, rather than just to the cerium ingredient. Some of the coupling between the magnetic moments of the different ions may be due to "orbital valence," since the mutual energy of two ions certainly depends on the relative orientation of their orbital angular momentum vectors. The orbital coupling is likewise capable of description by a molecular field in the first approximation.[20] Thus, strictly speaking, $-\gamma I'$ represents the field arising from both exchange and orbital coupling. The constant of proportionality γ turns out to be positive in tysonite. This is the common sign behavior for non-ferromagnetic bodies and means that the molecular field has a demagnetizing effect, since then $H-\gamma I'<H$. In a crystal such as tysonite the concentration of paramagnetic ions is, of course, much greater than for the hydrated sulphates. Hence it is not unreasonable that the exchange correction should be appreciable in

---

[18] J. Becquerel and W. J. de Haas, addendum to supplement 74 of the Leiden Communications.

[19] H. A. Kramers, Proc. Amsterdam Acad. **33**. 959 (1930).

[20] The subject of orbital coupling will be discussed more fully in a future paper by the writer. Cf. also H. A. Kramers, Physica **1**, 182 (1934). It is to be clearly understood that the exchange integrals themselves depend on the alignment of the orbital angular momentum vectors; in fact this dependence is perhaps the most important manifestation of orbital coupling.

tysonite though it is known to be negligible in $Gd_2(SO_4)_3 8H_2O$ even at 1.4°K.[21]

In the discussion of magnetic data, it is often convenient to use in place of the susceptibility the effective Bohr magneton number defined by

$$n_B^2 = 3k\chi(T+\Delta)/N\beta^2. \qquad (16)$$

The relation between V and χ, established in the preceding section, shows that in tysonite, n_B is then given in terms of the Verdet constant V by the relation

$$n_B^2 = -2.91\,V(T+\Delta). \qquad (17)$$

One must use in (16) and (17) only the values of V and χ appropriate to weak fields, where saturation can be neglected. If there is no saturation, we may replace the hyperbolic tangent by its argument in (15), and also we may consider the ratio of the intensity of magnetization to the effective field to be approximately proportional to $1/T$ at temperatures where the demagnetizing correction is appreciable. Hence

$$\gamma I'/(H-\gamma I') = \Delta/T, \qquad (18)$$

where Δ is a proportionality constant, and so

$$H-\gamma I' = H/(1+\Delta T^{-1}). \qquad (19)$$

Thus the effective magneton number should be a linear function

$$n_B^2 = 3\mu^2 + BT \qquad (20)$$

of T provided Eq. (15) is valid. The constant B equals $6k/\beta^2$ times the sum in the second term of (15). The linear relation (20) should hold up to at least the temperature of liquid hydrogen but, at still higher temperatures, more than one Kramers doublet becomes inhabited and then (15) and (20) cease to be valid.

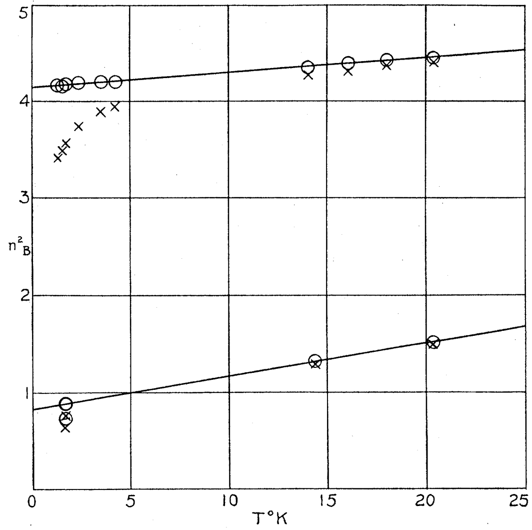

FIG. 1. Experimental values of the square of the effective Bohr magneton number n_B for tysonite at low temperatures, obtained from the data of Becquerel and de Haas by means of Eq. (17). The crosses are for $\Delta = 0$; the circles for $\Delta = 0.29$. The upper curve and corresponding points relate to the parallel component; the lower to the perpendicular component.

The values of n_B^2 deduced with the aid of (17) from Becquerel's data on the Verdet constants of tysonite are shown in Fig. 1. It is seen that with $\Delta = 0.29$ there is the desired linearity (20) but that if $\Delta = \gamma = 0$ there are pronounced deviations from linearity. Hence the introduction of the demagnetizing molecular field γ has been necessary in order to secure the proper variation with temperature for small T. In drawing Fig. 1 we have been aided by a letter from Professor Becquerel[17] informing us of new measurements on $V_{||}$. He has independently concluded that introduction of a demagnetizing field is necessary to secure the proper linearity (20) at low temperatures and finds that 0.29 is the best choice for Δ, which we hence adopt. Prior to his letter we had obtained $\Delta = 0.17$ on the basis of the older data and less thorough examination of the numerical fitting.

The determination of Δ for the perpendicular component is less certain, because here the experimental error is considerable. Note particularly the large divergence between the points at 1.7°K. If the values for $V_\perp$ at 14.3,

---

[21] According to P. W. Selwood, J. Am. Chem. Soc. **55**, 4869 (1933), the value of Δ in $GdCl_3$ is 14°. This, however, is not necessarily inconsistent with a Δ of only 0.29 in tysonite as gadolinium has a much larger spin vector **s**. Because only the component of spin along the total angular momentum **j** is effective with wide multiplets, the relation connecting Δ with the exchange integral J per electron can be shown to be

$$\Delta = -2Jz(\mathbf{s}\cdot\mathbf{j})^2/3kj^2 = -Jz(s^2+s+j^2+j-l^2-l)^2/6kj(j+1).$$

Here z is the number of paramagnetic neighbors possessed by an ion. If this formula is used, and if J is the same in tysonite as in $GdCl_3$, the value of Δ should be 88.2 times larger for the latter than for the former. Actually J should be larger in tysonite than in $GdCl_3$ because the Gd and Cl ions are larger than those of Ce, F, respectively, and because the greater nuclear charge of Gd than of Ce tends to reduce the overlapping of the wave functions.

20.3°K and the higher value for 1.7°K be accepted as accurate, $\Delta_\perp$ is 0.62. This value is, however, probably too high and in the absence of more accurate measurements, we shall in the following sections take Δ as having the same value for the parallel and perpendicular components. If this is done, it is seen that a fairly good fit for the perpendicular components can still be obtained if the straight line be drawn slightly above some of the points and below others, as shown by the circles in Fig. 1. If the molecular field arises predominantly from exchange rather than orbital coupling, one may take $\gamma_{||}=\gamma_\perp$ inasmuch as the proportionality constant γ is independent of direction in Heisenberg's theory. Since the left side of (18) is approximately $\gamma I'/H$ the values of Δ for the two axes should then obey the relation

$$\Delta_{||}/\Delta_\perp=\chi_{||}'/\chi_\perp', \qquad (21)$$

where $\chi'=I'/H$ refers to the total magnetic susceptibility of tysonite. Unfortunately, no information is available concerning $\chi_{||}'/\chi_\perp'$, since the ratio of the Verdet constants for the two axes supplies us only with the ratio $\chi_{||}/\chi_\perp$ for the part χ of the susceptibility due to the cerium ions only. As cerium is only one of the paramagnetic constituents of the mixed crystal tysonite, there is no reason why $\chi_{||}'/\chi_\perp$ should equal $\chi_{11}/\chi_\perp$. At helium temperatures, $\chi_{||}/\chi_\perp$ is about 5 but it is not unlikely that $\chi_{||}'/\chi_\perp'$ is smaller, since some of the other magnetic ingredients may behave more isotropically than cerium. Our choice unity for the ratio (21) seems about as reasonable as any which can be made at present, especially since Eq. (21) ceases to be valid when one considers the effect of directional valence on coupling between atoms.[22]

4. Saturation Effects in Tysonite

Instead of using Eq. (20) appropriate to weak fields, one can also deduce the numerical magnitude of the effective magneton number $n_B=3^{\frac{1}{2}}\mu$ at $T=0$ from the curvature of the graph of the rotation against field strength at a particular, very low temperature. This other, independent method based on saturation is that used by Kramers and Becquerel. At helium temperatures, the second term of (15) is of negligible importance, and the ratio of the rotations at two different field strengths will fix μ even if one assumes (2) instead of (3). Before one can use (15) it is necessary to make the assumption that the demagnetizing field $-\gamma I'$ is proportional to the paramagnetic rotation ρ, so that

$$H-\gamma I'=H-b\rho, \qquad (22)$$

where b is a constant. The value of Δ is then connected with that of b by the relation

$$\Delta=b\rho_\infty\mu\beta/k$$

if ρ_∞ denotes the rotation at infinite field strengths, where the hyperbolic tangent may be replaced by unity. The assumption (22) may not entail serious error but certainly is not entirely correct, since the Faraday rotation ρ arises almost entirely from the cerium ions and so represents, except for a constant factor, the intensity of magnetization I of the cerium alone. On the other hand the demagnetizing field is proportional to the total intensity of magnetization I' of the mixed crystal. There is no reason why I' and I should be exactly the same functions of H, but possibly the difference between the two functions is not large.

If we assume (22) and that $\Delta=0.29$, Becquerel finds[17] that the value obtained from his latest saturation curves is $\mu=1.288$. The corresponding value obtained from (17) and (20), i.e., from the intercept in Fig. 1, is $\mu=1.18$. The agreement between the two methods is thus only moderate. The estimate obtained from the saturation effect is reduced to 1.22, thus removing a large part of the discrepancy, if one makes the approximation (19) rather than (22) in the argument of the hyperbolic tangent even at high field strengths. Eq. (22) would be an allowable approximation if one assumed that most of the magnetization of the mixed crystal arose from ions which do not exhibit appreciable saturation even at the highest field strength employed, so that I' is a nearly linear function of H even though I exhibits appreciable curvature. How-

---

[22] In terms of the vector model, the coupling energy connecting two ions a, b has the form $\Sigma_{i,k}c_{ik}j_i{}^a\cdot j_k{}^b$ where $j_1{}^a$, $j_2{}^a$, $j_3{}^a$ are the components of the angular momentum of ion a along the three coordinate axes (cf. Kramers, reference 20). A simple calculation shows that the constant γ of the molecular field is approximately proportional to c_{ii} if H is applied along the direction of axis i. If we ignore orbital valence, as in Heisenberg's theory, then $a_{11}=a_{22}=a_{33}$, but actually the orbital effects may make $a_{11}\neq a_{22}$, etc. Then $\gamma_{||}\neq\gamma_\perp$, and so (21) ceases to be valid.

ever, it is hard to see any reason why I' should exhibit much less curvature than I, since the other paramagnetic ions in the crystal, unless they greatly outnumber the cerium ions, must have approximately as great values of μ and hence as much curvature as the cerium if they are to be important contributors to the magnetization.

In the case of the perpendicular component, the situation is still less encouraging. In the first place there is the difficulty that the experimental data are self-contradictory, for the experimental values of $V_\perp$ depend even in weak fields on the direction chosen for observation in the plane perpendicular to the crystal axis. Any sort of theory,[23] however, shows that such a variation is incompatible with the hexagonal symmetry of the crystal. (We shall later see, in section 6, that there might be some variation with direction in the saturation method but that this is too small to be appreciable at the field strengths used.) When we give experimental data or theoretical calculations aimed to fit these data on the perpendicular component near $T=0$ we shall always give two values. The first of these is based on measurements parallel to one of the diagonal axes of the crystal. The second of these will be inclosed in parentheses and is based on measurements still perpendicular to the crystallographic axis but at an angle of about 30° to the diagonal axis. The first and second directions are equivalent to horizontal and vertical axes in Fig. 3 of section 6. The difference between the two sets of measurements is perhaps due to crystalline flaws or to the fact that Becquerel used two different crystals. It disappears at hydrogen temperatures and higher.

With $\Delta=0.29$, the value of $\mu_\perp$ furnished by the saturation method is 0.874 (0.726) while (17) yields 0.523 (0.469). In connection with the saturation procedure, it makes little difference whether one uses (19) or (22), since in the perpendicular component only the beginnings of saturation are observed. Part of the trouble may easily be experimental error, since the saturation curvature in the perpendicular direction is slight and hence very difficult to determine. We shall show in section 6 that the value of $\mu_\perp$ obtained by the saturation method is reduced to 0.780 (0.726), if all the cerium atoms do not have the same crystallographic situations, in which case Eq. (15) must be modified.

In testing various types of crystalline fields in the next two sections, we shall use the values of n_B furnished by (17) rather than by the saturation curvature, since the former appear to be the more reliable. The discrepancy between the two methods of determining n_B is inherent in the existing data, and for the following reason cannot possibly be imputed to our use of (1) (i.e., correlation of the temperature variation of χ with that of V) rather than of the less drastic conventional hypothesis (2). Suppose that we admitted only (2) and assumed that saturation methods were reliable. Then the effective "powder" magneton number $(\mu_{||}^2+2\mu_\perp^2)^{\frac{1}{2}}$ would be deduced from saturation to be 1.78 (1.65) at 1.7°. On the other hand it is known from susceptibility measurements that n_B for CeF_3 powder has already dropped to 1.52 at 14.48°K. Now it is scarcely conceivable that the magneton number should actually increase as one lowers the temperature from 14.48° to 1.7°. In fact, examination of Fig. 2 shows that any reasonable sort of extrapolation of the direct experimental measurements of susceptibilities, indicated by crossed circles in Fig. 2, to very low temperatures demands that n_B be about 1.4 for the powder near $T=0$. We thus appear forced to accept the lower values of n_B given by (17) in preference to the greater values yielded by saturation.

Of course it is possible that the trouble may lie in a real difference between CeF_3 and tysonite for our purposes. The constancy of the ratio χ/V in Table I makes it appear probable that if the two materials are unlike, they manifest approximately the same percentage difference in their susceptibilities at all temperatures. If so, our use of (17) may be regarded as a convenient and allowable way to extend the data on CeF_3 to individual axes and very low temperatures. Our calculations in sections 5 and 6 would then be for the crystalline potential of CeF_3 rather than of tysonite. Because of the qualitative similarity of the two substances, our ensuing conclusions concerning the relative merits of the triclinic and staggered rhombic fields would also apply to tysonite.

---

[23] J. H. Van Vleck, Phys. Rev. **45**, 115 (L) (1934).

5. Failure of a Triclinic Field to Represent the Measurements in Tysonite

So far our discussion has consisted mostly in establishing the proportionality between χ and V. We now propose to examine what crystalline field will represent the observed behavior of χ, or equally well the related V. We thus enter upon a subject whose broader aspects have been developed by Kramers,[3] Bethe,[7] Penney,[8] Schlapp[8] and Van Vleck.[9] The only attempt at numerical calculations for tysonite has been made by Kramers.[24] When we refer to his work, we always mean his most recent paper[24] and not his earlier articles[3] on tysonite which involved the incorrect assumption that the multiplet width structure is small compared to the crystalline potential.

Tysonite is a hexagonal crystal, but this does not mean that the field on an individual atom possesses hexagonal symmetry. Instead the hexagonal symmetry need be achieved only from a macroscopic point of view. The x-ray measurements of Oftedal[15] indicate that the fields acting on individual atoms have nearly triclinic symmetry, i.e., nearly a period of 120° around the crystallographic axis. The simplest assumption, and the one made by Kramers,[24] is that these fields can be considered accurately triclinic. This facilitates the calculations, for the off-diagonal matrix elements of the crystalline potential are then entirely of the form $\Delta M = \pm 3$, with none between $M = 3/2$, $M = -3/2$. Here M denotes the magnetic quantum number associated with spatial quantization relative to the crystallographic symmetry. The wave functions belonging to the Stark levels are then of the form

$$\Psi_{\pm\mathrm{I}} = \alpha\psi_{\pm5/2} + (1-\alpha^2)^{1/2}\psi_{\mp1/2},$$
$$\Psi_{\pm\mathrm{II}} = (1-\alpha^2)^{1/2}\psi_{\pm5/2} - \alpha\psi_{\mp1/2},$$
$$\Psi_{\pm\mathrm{III}} = \psi_{\pm3/2}, \qquad (23)$$

where α is a constant and the fractional subscripts relate to M. The two sign choices yield the two components of a Kramers doublet. Kramers gives the formula for the mean χ corresponding to (23) and we need not repeat it here. He does not explicitly isolate $\chi_{\parallel}$, $\chi_{\perp}$ but this can be done without difficulty.

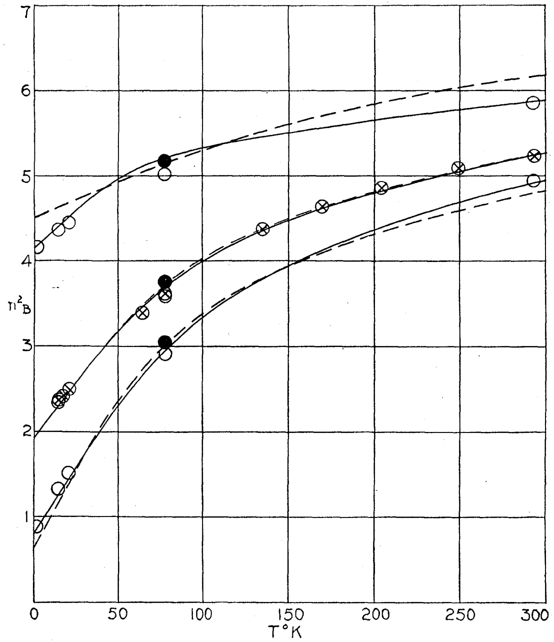

Fig. 2. The square of the effective Bohr magneton number as a function of temperature. The crossed circles ⊗ are experimental values deduced from Leiden susceptibility measurements on CeF$_3$ by means of (16) with $\Delta = 0.29$, while the plain circles ○ give values obtained from the data of Becquerel and de Haas on the magnetic rotation of tysonite (with adjustment at 293°K mentioned in section 2). The solid circles ● at 77°K are obtained by using $K = 0.67 \times 10^{-3}$ instead of $K = 0$ in (1) and (17). The broken lines are theoretical curves based on Kramers' triclinic field, with constants chosen as in (25). The solid curves are for the staggered rhombic field described in section 6. The upper and lower curves refer, respectively, to directions parallel and perpendicular to the optic axis. The middle curve relates to the mean.

Kramers considered only the mean or powder susceptibility of CeF$_3$, which he shows can be fitted quite well with the following choice of constants

$$\alpha^2 = 2/3, \quad W_{\mathrm{III}} - W_{\mathrm{I}} = 163 \text{ cm}^{-1},$$
$$W_{\mathrm{II}} - W_{\mathrm{I}} = 4 \times 163 \text{ cm}^{-1}. \qquad (24)$$

(Here and elsewhere we take the lowest Stark component as the origin of energy.) When, however, the proportionality between magnetic susceptibility and rotation is used, the measurements extend down to 1.5° rather than 14.3°K, and especially, data for individual crystalline axes become available. The test to be met by the theory then becomes considerably more

---

[24] H. A. Kramers, Proc. Amsterdam Acad. **36**, 1 (1933).

severe and it turns out that no wave functions of the form (23) are adequate. It is possible, to be sure, to represent the mean susceptibility over the entire range $1.5-293°\text{K}$ by modifying slightly Kramers' choice of the constants as follows

$$\alpha^2=0.644, \quad W_{\text{III}}-W_{\text{I}}=139 \text{ cm}^{-1}, \quad W_{\text{II}}-W_{\text{I}}=5.5\times 139 \text{ cm}^{-1}. \tag{25}$$

However, the susceptibilities for individual axes are not then correctly represented as can be seen from examination of the broken lines in Fig. 2. Kramers notes that the powder susceptibility of CeF_3 can be fitted by still another choice of constants, which is similar to (24) except that W_{II}, W_{III} are interchanged. This or any neighboring choice of constants, however, gives even worse agreement on individual axes than does (25). It would require that n_B for the parallel component reach a maximum at around 500–600°K and then decline as the temperature is raised further.

This failure of purely triclinic fields is not surprising, for the following reason. If there is a center of symmetry the terms of the crystalline potential which yield matrix elements of the form $\Delta M=\pm 3$ arise, as Kramers shows, only from Tesseral harmonics of even order which change sign under reflection in the equatorial plane (e.g., T_4^3, T_6^3, etc.). Without such elements we can only have $\alpha=0$ or $\alpha=1$ in (23); i.e., wave functions of the same form as for a field of axial symmetry. Furthermore, the calculation of the susceptibility for a field of axial symmetry is particularly simple, and one easily convinces oneself that the data on the individual susceptibilities of tysonite are incapable of representation by a field of axial symmetry: in fact even the mean is fitted none too well. To give a situation like (24), the matrix elements $\Delta M=\pm 3$ must be quite important, and this in turn demands large terms in the harmonic expansion of the crystalline potential which change sign under equatorial reflection. However, according to the crystallographic structure tentatively proposed by Oftedal,[15] there is a plane of symmetry passing through each atom perpendicular to the crystallographic axis. If this is the case and if there is triclinic symmetry, there can be no such terms in the expansion of the potential function. Oftedal himself mentions that the crystallographic structure may be somewhat distorted from the diagrams which he gives. In fact, he even mentions the possibility that the atoms do not have planes of symmetry in their potential fields. This will be the case if the corresponding crystallographic planes "above" and "below" a given atom are not equidistant. However, one would expect any asymmetries of this type to be small, so that it seems rather unreasonable for surface harmonics which are odd under equatorial reflection to have as large an effect as postulated by Kramers.

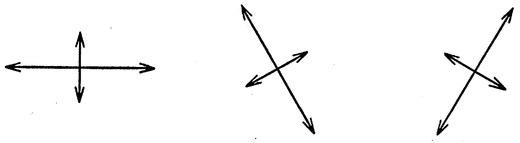

FIG. 3. "Staggered" rhombic field, representing the three orientations of the local field about an individual Ce^{+++} ion.

6. REPRESENTATION OF THE SUSCEPTIBILITY OF TYSONITE BY A STAGGERED RHOMBIC FIELD

Instead of a trigonal field, we may essay calculations on the assumption that each atom is subject to a field of rhombic symmetry. One of the principal rhombic axes, *viz.*, the z axis, we shall suppose to be always parallel to the crystallographic or optic axis. One-third of the atoms will have their x and y axes directed in each of the fashions shown in Fig. 3, so that the field for one atom will differ from that of another only by a rotation through 120°, thus explaining our use of the term "staggered." A staggered structure of this type is precisely what is indicated in the tentative structure diagram for tysonite published by Oftedal. Hence our model is perhaps more reasonable than the triclinic one used by Kramers; we must, however, mention that to represent the susceptibility properly, the "rhombic" terms which represent the departures from effective axial symmetry (represented symbolically in Fig. 3 by the difference in length of the crossed arrows) turn out to be surprisingly large, greater than one would *a priori* expect from the nearly triclinic symmetry in ionic surroundings reported by Oftedal.

The matrix elements introduced by a field of rhombic symmetry are of the form $\Delta M = M' - M'' = 0$, ± 2, ± 4 so that the wave functions may be taken to be

$$\Psi_{i\pm} = \alpha^i{}_{5/2}\psi_{\pm 5/2} + \alpha^i{}_{1/2}\psi_{\pm 1/2} + \alpha^i{}_{-3/2}\psi_{\mp 3/2}, \qquad i = \mathrm{I, II, III}. \tag{26}$$

As previously, the two sign choices give the two components of a Kramers doublet. We have assumed the α's to be real, which involves no loss of generality since by proper choice of phases the matrix elements of the crystalline potential may all be made real if there is rhombic symmetry. The coefficients α are not all independent and must satisfy the orthogonality and normalization relations

$$\alpha^i{}_{5/2}\alpha^j{}_{5/2} + \alpha^i{}_{1/2}\alpha^j{}_{1/2} + \alpha^i{}_{-3/2}\alpha^j{}_{-3/2} = \delta_j{}^i. \tag{27}$$

In a system of representation appropriate to the wave functions (26), the matrix elements of the magnetic moment are

$$\mu_z(i\pm; j\pm) = g\left[\frac{5}{2}\alpha^i{}_{5/2}\alpha^j{}_{5/2} + \frac{1}{2}\alpha^i{}_{1/2}\alpha^j{}_{1/2} - \frac{3}{2}\alpha^i{}_{-3/2}\alpha^j{}_{-3/2}\right], \tag{28}$$

$$\mu_x(i\pm; j\mp) = g\left[\frac{5^{1/2}}{2}(\alpha^i{}_{5/2}\alpha^j{}_{-3/2} + \alpha^i{}_{-3/2}\alpha^j{}_{5/2}) + 2^{1/2}(\alpha^i{}_{1/2}\alpha^j{}_{-3/2} + \alpha^i{}_{-3/2}\alpha^j{}_{1/2}) + \frac{3}{2}\alpha^i{}_{1/2}\alpha^j{}_{1/2}\right] \tag{29}$$

$$\begin{aligned} -\mu_y(i-; j+) = \mu_y(i+; j-) = (-1)^{1/2} g\biggl[&\frac{5^{1/2}}{2}(\alpha^i{}_{5/2}\alpha^j{}_{-3/2} + \alpha^i{}_{-3/2}\alpha^j{}_{5/2}) \\ &- 2^{1/2}(\alpha^i{}_{1/2}\alpha^j{}_{-3/2} + \alpha^i{}_{-3/2}\alpha^j{}_{1/2}) + \frac{3}{2}\alpha^i{}_{1/2}\alpha^j{}_{1/2}\biggr]. \end{aligned} \tag{30}$$

These expressions follow from the well-known relations

$$(\mu_x \pm i\mu_y)(M; M\mp 1) = g[J(J+1) - M(M\mp 1)]^{1/2}, \qquad \mu_z(M; M) = g\beta M$$

characteristic of the usual M system of representation appropriate to a field of axial symmetry. Elements of the form $\mu_z(i\pm; j\mp)$, $\mu_x(i\pm; j\pm)$, $\mu_y(i\pm; j\pm)$ all vanish.

By standard principles of quantum magnetic theory, the square of the effective magneton number for the z direction in weak fields is

$$n_B{}^2(z) = \frac{3\Sigma_i\{\,|\mu_z(i+; i+)|^2 + 2kT\Sigma_{j\neq i}|\mu_z(i+; j+)|^2/(W_j{}^0 - W_i{}^0)\}e^{-W_i{}^0/kT}}{\Sigma e^{-W_i{}^0/kT}}. \tag{31}$$

The expressions for the x and y components are similar except that μ_x or μ_y replaces μ_z and that the indices are $(i+; i-)$, $(i+; j-)$ instead of $(i+; i+)$, $(i+; j+)$. Eq. (31) contains only one sign choice, as the summation over the two components of the Kramers doublet has already been performed.

The constants at our disposal must now be adjusted so as to yield agreement with experiment. These constants are five in number, *viz.*, the energy intervals $W_{\mathrm{II}}{}^0 - W_{\mathrm{I}}{}^0$ $W_{\mathrm{III}}{}^0 - W_{\mathrm{I}}{}^0$ and three of the coefficients α. Only three of the nine α's are arbitrary because of the six constraints imposed by (27). In place of $W_{\mathrm{II}}{}^0 - W_{\mathrm{I}}{}^0$, $W_{\mathrm{III}}{}^0 - W_{\mathrm{I}}{}^0$ it is convenient to introduce new parameters q, A defined by $W_{\mathrm{II}}{}^0 - W_{\mathrm{I}}{}^0 = A$, $W_{\mathrm{III}}{}^0 - W_{\mathrm{I}}{}^0 = qA$. If we plot $n_B{}^2$ against T, the effect of changing A is merely to expand or contract the scale of abscissa. There are obviously more complexity and more leeway in adjustment to experiment than in Kramers' triclinic case, where there were three adjustable constants. It should not, however, be inferred that with a rhombic field agreement can be achieved with almost any sort of experimental curve, for with data on two principal axes the material to be fitted is considerable. In fact most of the parameters are fixed simply by data in the hydrogen-helium range.

The simplest way to start is to fit the experimental values of the effective magneton number defined by (20) at $T=1.7°$, which is the same as $T=0$ to all intents and purposes. Using values appropriate to $\Delta=0.29$ quoted in section 4, we thus have

$$\mu_z(\mathrm{I}^+;\mathrm{I}^+)=\mu_{||}=1.18,\quad \tfrac{1}{2}[|\mu_x(\mathrm{I}^-;\mathrm{I}^+)|^2+|\mu_y(\mathrm{I}^-;\mathrm{I}^+)|^2]=\mu_\perp^2=(0.52)^2,\quad (\text{or } (0.47)^2) \tag{32}$$

with notation as in (27), (28), (29). The value of $\frac{1}{2}(\mu_x^2+\mu_y^2)$ is the same as that of $\mu_\perp^2$ because one must average over the three types of orientation of rhombic axes shown in Fig. 3. It is found that there are four sets of values of α^{I} which will fit (32), *viz.*

$$\alpha^{\mathrm{I}}{}_{5/2}=0.762,\ (0.736),\qquad \alpha^{\mathrm{I}}{}_{1/2}=0.525,\ (0.592),\qquad \alpha^{\mathrm{I}}{}_{-3/2}=-0.379,\ (-0.327), \tag{33}$$

$$\alpha^{\mathrm{I}}{}_{5/2}=0.122,\ (0.145),\qquad \alpha^{\mathrm{I}}{}_{1/2}=0.187,\ (0.152),\qquad \alpha^{\mathrm{I}}{}_{-3/2}=0.975,\ (0.978), \tag{34a}$$

$$\alpha^{\mathrm{I}}{}_{5/2}=0.095,\ (0.126),\qquad \alpha^{\mathrm{I}}{}_{1/2}=0.217,\ (0.182),\qquad \alpha^{\mathrm{I}}{}_{-3/2}=-0.972,\ (-0.975), \tag{34b}$$

$$\alpha^{\mathrm{I}}{}_{5/2}=0.680,\ (0.700),\qquad \alpha^{\mathrm{I}}{}_{1/2}=0.713,\ (0.675),\qquad \alpha^{\mathrm{I}}{}_{-3/2}=-0.167,\ (-0.234). \tag{35}$$

As explained in section 4, values in parenthesis relate to a choice of 0.47 rather than 0.52 for the experimental value of $\mu_\perp$.

The remaining constants are determined so as to fit the experimental data at higher temperatures and to yield proper values for the constant B in formula (20) at low temperatures. One relation between these other constants is immediately obtained by giving the ratio $B_\perp/B_{||}$ the proper value. This ratio has the advantage of being independent of the scale factor A. Too much reliance should not, however, be placed on endeavors to fit this ratio exactly, as experimentally it is not known with much precision because of uncertainty in the value of Δ for the perpendicular component. Nevertheless, study of the approximate magnitude of this ratio furnishes fairly conclusive evidence against the Kramers' triclinic field studied in section 5, since (25) yields a value 4.4 for $B_\perp/B_{||}$ which is excessively high compared with the experimental value 2.3.

It is impossible to choose the other constants so as to give good agreement with experiment if one uses (34a), (34b), or (35). It is disappointing that (34a), (34b) must thus be excluded, for wave functions of the type (34a) or (34b) would require only slight departures of the crystalline potential from axial symmetry, where the matrix of the α's is unity. No nearly axial field can be successful, since a perfectly axial field yields an infinite value of $B_\perp/B_{||}$.

With (33), the experimental data in weak fields can be fitted quite well for both the parallel and perpendicular components if one chooses the constants as follows for the upper states:

$$\alpha^{\mathrm{II}}{}_{5/2}=0.517,\qquad \alpha^{\mathrm{II}}{}_{1/2}=-0.846,\qquad \alpha^{\mathrm{II}}{}_{-3/2}=-0.134\qquad W_{\mathrm{II}}{}^0-W_{\mathrm{I}}{}^0=130\ \mathrm{cm}^{-1}, \tag{36}$$

$$\alpha^{\mathrm{III}}{}_{5/2}=0.391,\qquad \alpha^{\mathrm{III}}{}_{1/2}=0.095,\qquad \alpha^{\mathrm{III}}{}_{-3/2}=0.916,\qquad W_{\mathrm{III}}{}^0-W_{\mathrm{I}}{}^0=754\ \mathrm{cm}^{-1}. \tag{37}$$

These values have, of course, been chosen in compliance with (27). The curves for the effective magneton number based on (33), (36), (37) are indicated by solid lines in Fig. 2 and are seen to agree with experiment better than do those for triclinic fields.

For simplicity, we have shown for the perpendicular component in Fig. 2 only the theoretical curves which are fitted to a value 0.523 for $\mu_\perp$ at $T=0$. If the experimental value is instead taken as 0.469, we would have to use the second set of constants in (33) and modify slightly the constants in (36), (37) and (25). These alterations, however, are not as important as in the discussion of saturation, and do not affect the conclusion that the staggered rhombic field fits the data better than does the triclinic.

Saturation for the perpendicular component. Since we must average over the three types of rhombic axes shown in Fig. 3, Eq. (15) does not yield directly the susceptibility for directions perpendicular to the crystallographic axis. Let us suppose that the magnetic field is applied perpendicular to this axis and makes an angle φ with one of the long axes in Fig. 3. Then one can show that the corresponding type of atoms in Fig. 3 has first order Zeeman energies for the lowest Kramers doublet of the form

$$W=W_0\pm H\beta\mu(\phi) \qquad \text{with} \qquad \mu(\phi)=(\mu_x^2\cos^2\varphi+\mu_y^2\sin^2\varphi)^{1/2}.$$

The formulas for the other two types of atoms are, of course, similar except that ϕ must be advanced by $2\pi/3$ or $4\pi/3$. Hence the proper formula for $\chi_\perp(\varphi)$ is

$$\chi_\perp(\varphi)=\frac{N\beta}{3H}\Sigma_{\psi=0,\ 2\pi/3,\ 4\pi/3}\quad \mu(\varphi+\psi)\tanh\left[\frac{\mu(\varphi+\psi)\beta(H-\gamma I')}{kT}\right]$$
$$+2N\frac{(H-\gamma I')}{H}\Sigma_{n'(n'\neq n)}\frac{|m_x(n';n)|^2+|m_y(n';n)|^2}{2h\nu(n';n)}. \tag{38}$$

One notes that (38) is not independent of φ and immediately wonders whether this is the reason why Becquerel observes different rotations for $\varphi=0$ and $\varphi=30°$ (cf. section 4). Such an explanation, however, will not work, since if (38) is expanded as a Taylor's series in H, only the coefficients of H^4 and higher powers depend upon φ. At the field strengths used by Becquerel, little harm is done if the development is terminated at H^2 and if we neglect terms of the order $H^2\Delta^2$. Then (38) reduces to an expression[25]

$$\chi_\perp=\frac{N\beta^2}{k(T+\Delta)}\left[\frac{\mu_x^2+\mu_y^2}{2}\right]-\frac{N\beta^4H^2}{k^3T^3}\left(\frac{1}{3}-\frac{4\Delta}{3T}+\cdots\right)\left[\frac{(\mu_x^2+\mu_y^2)^2}{4}+\frac{(\mu_x^2-\mu_y^2)^2}{8}\right] \tag{39}$$

independent of φ. In writing (39), we have dropped the second or "high frequency" part of (38); this is allowable at very low temperatures, where saturation is important. As already stated, and as is also apparent from (39), the value of the effective magneton number appropriate to weak fields is $3^{1/2}\mu_\perp=[3(\mu_x^2+\mu_y^2)/2]^{1/2}$. Because of the term in $\mu_x^2-\mu_y^2$, the coefficient of H^2 in (39) is not the same as that which would be obtained by expanding (15) with $\mu=\mu_\perp$. When Becquerel measures the saturation curvature in the Faraday rotation at low temperatures, he determines empirically the ratio of the coefficient of H^2 to the term independent of H in $\chi_\perp$. The effect of the rhombic staggering is to make this ratio greater by a factor

$$a^2=1+\tfrac{1}{2}[(\mu_x^2-\mu_y^2)/(\mu_x^2+\mu_y^2)]^2 \tag{40}$$

than it would be if we used Eq. (15). Thus the saturation method really furnishes us with $a\mu_\perp$ rather than $\mu_\perp$, if inadvertently (15) is used, as is usually done. When this distinction is overlooked, the apparent values of $\mu_\perp$ furnished by saturation will thus be greater than those yielded by the Eq. (17) appropriate to weak fields. With the choice of constants (33), the magnitude of a is found from (29, 30) and (40) to be 1.12 (1.00). When (38) rather than (15) is used, the value of $\mu_\perp$ furnished by the saturation method is then reduced from 0.874 (0.726) to 0.780 (0.726). Hence the correction (40) removes part, but not all, of the discrepancy with the value 0.523 (0.469) deduced from (17) in section 4, provided we prefer the determinations not in parentheses.

With a triclinic instead of staggered rhombic field, not even a part of the discrepancy can be removed, since in the triclinic case no averaging over different types of atoms is necessary, and (15) can be used even for the perpendicular component.

Constants of the rhombic crystalline field. Let us suppose that the crystalline potential is developed as a series

$$V=\Sigma_{l,\,m}f_l^m(r)Y_l^m(\theta,\varphi) \tag{41}$$

in Tesseral harmonics $Y_l^m(\theta,\varphi)=F(\theta)e^{im\varphi}$ which we suppose normalized to unity. Because of the

---

[25] In deriving (39) from (38) one must remember that γ is involved implicitly through I' on the right side of (38) as well as explicitly. Otherwise the factor 4/3 multiplying Δ in (39) would be wanting.

rhombic holohedral symmetry, f_l^{-m} equals f_l^m and the coefficients vanish unless l and m are both even. If V satisfies Laplace's equation then $f_l^m(r) \sim r^l$. The Laplacian of V probably vanishes only approximately, since V, as we use it, is inclusive of the effect of the charge redistribution of the $5s^2 5p^6$ shell under the influence of the interatomic field, and so V may have a charge source even in the region occupied by the $4f$ orbits inasmuch as the inner parts of $5s$, $5p$ overlap $4f$. We wish to show that only certain choices of the coefficients in (41) will lead to wave functions and energy levels of the structure (33), (36), (37). In the "M" or axial system of representation, one finds by the Kramers' symbolic method,[26] or otherwise, that the matrix representing the potential (41) is

$$\begin{array}{r|ccc|}
\pm 5/2 & A_0^0+(A_2^0/6^{\frac{1}{2}})+(A_4^0/70^{\frac{1}{2}}) & (A_2^2/10^{\frac{1}{2}})-(3A_4^2/70^{\frac{1}{2}}) & A_4^4/5^{\frac{1}{2}} \\
\pm 1/2 & (A_2^2/10^{\frac{1}{2}})-(3A_4^2/70^{\frac{1}{2}}) & A_0^0-(4A_2^0/150^{\frac{1}{2}})+(2A_4^0/70^{\frac{1}{2}}) & (3A_2^2/50^{\frac{1}{2}})+(A_4^2/14^{\frac{1}{2}}) \\
\mp 3/2 & A_4^4/5^{\frac{1}{2}} & (3A_2^2/50^{\frac{1}{2}})+(A_4^2/14^{\frac{1}{2}}) & A_0^0-(A_2^0/150^{\frac{1}{2}})-(3A_4^0/70^{\frac{1}{2}})
\end{array} \qquad (42)$$

with $A_l^m = c_l \int_0^\infty f_l^m R^2 r^2 dr$, where c_l is a constant of proportionality independent of m and R is the radial wave function. Let $\boldsymbol{\alpha}$ be the matrix of the coefficients α and let $\mathbf{H}$ be a diagonal matrix of characteristic values W_{I}, W_{II}, W_{III}. After the crystalline potential is diagonalized, its matrix is $\mathbf{H}$. In the original M system, before this diagonalization, its matrix is $\boldsymbol{\alpha} H \boldsymbol{\alpha}^{-1}$ inasmuch as $\boldsymbol{\alpha}^{-1}$ is the inverse of the transformation from the axial to the final diagonal system of representation. Using (33), (36), (37), and the fact that $\boldsymbol{\alpha}^{-1}$ is the same as the "transpose" $\tilde{\boldsymbol{\alpha}}$ of $\boldsymbol{\alpha}$, one finds

$$\boldsymbol{\alpha}\mathbf{H}\boldsymbol{\alpha}^{-1} = \boldsymbol{\alpha}\mathbf{H}\tilde{\boldsymbol{\alpha}} = \left|\begin{array}{rrr} 150 & -29 & 261 \\ -29 & 100 & 80 \\ 261 & 80 & 634 \end{array}\right| \mathrm{cm}^{-1}. \qquad (43)$$

To obtain (33), (36), (37), the A's must be so chosen that (42) reduces to (43). The surprising feature is that the fourth order terms A_4 are thus seen to be fully as large as the second order ones A_2. Hence a second order rhombic field of the "asymmetrical top" type is entirely inadequate and the convergence of the Taylor's development of the potential is hence presumably poor, so that it is probably not allowable to terminate the development at the fourth order terms. When the higher order terms are included the identification of the A's ceases, of course, to be unique. A similar inadequacy of the second order terms is also found in the Kramers' triclinic theory, since α in (23) can differ from zero or unity only if fourth and higher order terms are admitted. Both in Kramers' theory and ours, the lowest diagonal element of the crystalline potential in the original axial system of representation belongs to $M = 3/2$. This situation is impossible with only second order terms. If the crystalline field had cubic symmetry we would have $A_2^0 = A_2^2 = A_4^2 = 0$; $A_4^0 = A_4^4 (14/5)^{\frac{1}{2}}$. Actually these relations are not fulfilled, as is not at all surprising, since actually tysonite has hexagonal rather than cubic symmetry. The deviations from fulfillment are on the whole remarkably small, for (43) would satisfy these cubic conditions if, for instance, we replaced the elements 150, 634, −29, 80 by 217, 685, 0, 0 respectively, leaving 100, 261 unaltered. This probably is only a fortuitous coincidence, but, of course, it is conceivable that the microscopic environment of a given ion show some vestiges of cubic symmetry even though macroscopically the crystal is hexagonal.

It will be noted that our procedure is in a certain sense the reverse of that used by Penney and Schlapp.[8] Instead of first postulating a given crystalline potential (41), and then calculating the susceptibility, we first find the structure of the wave functions and energy levels which will represent the observed susceptibility. Then we transform "backwards" to the M system in the fashion (43) to find the characteristics of the crystalline potential. It is believed that this alternative, reverse procedure may become increasingly advisable for other materials than

---

[26] H. A. Kramers, Proc. Amsterdam Acad. **33**, 953 (1930); **34**, 965 (1931).

tysonite as the magnetic theory becomes increasingly refined through the development of improved experimental data on individual principal susceptibilities, etc., permitting more drastic tests and presumably requiring more complicated potentials than the simple ones used in the first approximations.

In conclusion, we do not wish to give any impression of finality to the rhombic potential represented in (43). It does seem to work better than the triclinic, and is fully as compatible with the known facts of the crystallographic structure. The departures from axial symmetry involved in (43) are rather large, and it is possible that they can be reduced by considering still more complicated potentials, notably those involving simultaneously both triclinic and staggered rhombic terms. Another possible modification is to have the z axis of the rhombic system spiral about the optic axis instead of being parallel to the latter. Then to compute the susceptibility in any given direction, a three-dimensional averaging process is required, rather than a two-dimensional one as in (38) for the directions perpendicular to the optic axis and none at all for the parallel direction. The attractive feature of this modification is that it makes the magneton number deduced from saturation greater than that deduced from (17) even in the case of the parallel component, thus tending to alleviate the discrepancy between the two methods emphasized in section 4. Furthermore, the effect of the matrix elements of the crystalline potential and of the moment which are non-diagonal in the inner quantum number j ought really to be considered if the separation of $F_{5/2}$ and $F_{7/2}$ in cerium is only 1600 cm^{-1}, as reported by Brunetti and Ollano.[27] However, it appears useless to make elaborate calculations based on these various ideas until better experimental data are available for the perpendicular component.

---

[27] R. Brunetti and Z. Ollano, Zeits. f. Physik **75**, 415 (1932).

Nitrogen Molecular Spectra in the Vacuum Ultraviolet

William W. Watson and Philip G. Koontz, *Yale University*

(Received April 27, 1934)

Nitrogen molecular spectra in the region from 900A to 2300A have been photographed with a 10-foot vacuum spectrograph giving a dispersion of 5.5A/mm. Partial rotational quantum analyses have been made for several bands of the $a^1\Pi_u \rightarrow {}^1\Sigma_g^+$ system yielding the constants $B_0' = 1.632 \pm 0.002$, $B_0'' = 1.998 \pm 0.002$, $\alpha' = 0.021$, $\alpha'' = 0.018$. Many new bands in a nitrogen band system with an origin at 1847A discovered by Hopfield in a condensed discharge in a helium-nitrogen mixture are reported. This system is due to N_2^+, having the same lower state as that of the first negative system. The rôle of the helium is discussed. Birge and Hopfield's b' progression is found to consist of Q branches only with $B' = 1.147$. Several new N_2 ground state progressions among the bands in the 900A–1300A interval are presented.

INTRODUCTION

SEVERAL band systems assigned to the N_2 or N_2^+ molecules lie in the vacuum ultraviolet. The vibrational structure of the prominent $a^1\Pi_u \rightarrow {}^1\Sigma_g^+$ system, which extends through the whole Schumann region, has been investigated in detail by Birge and Hopfield.[1] Their analysis yielded accurate vibrational energy data for these two N_2 states, but the dispersion of their spectrograph was insufficient to reveal the rotational structure of the bands. That the upper state of this system is really ${}^1\Pi_u$ has been proved by Appleyard[2] who has made a rotational quantum analysis of the (5,13) and (5,14) bands which may be photographed with a spectrograph in air. The only determination of the rotational energy constant B_0 for the normal ${}^1\Sigma_g^+$ state, however, has been that of Rasetti[3]

---

[1] R. T. Birge and J. J. Hopfield, Astrophys. J. **68**, 257 (1928).

[2] E. T. S. Appleyard, Phys. Rev. **41**, 254 (1932).

[3] F. Rasetti, Phys. Rev. **34**, 367 (1929).