Eq. (1) is not valid, the lines K 4044 and 4047 have been included in Table I. For higher series lines, $\Delta\nu$ may have a large positive range, and therefore $I'(\nu)$ may contain appreciable "blue" intensities. The present treatment is entirely inadequate for dealing with the highest series members of the alkali spectra, where the atom in its excited state embraces thousands of perturbers.[14]

While this work was in progress there has appeared a paper by Minkowski[15] in which the intensity distribution of the $D$ lines perturbed by small pressures of $A$ is investigated and compared with the results of Lenz[5] and Kuhn.[6] The agreement is found satisfactory. The considerations here presented do not conflict with these results in their respective ranges of validity (cf. in particular the remarks on the limiting form of Eq. (18)), and hence are not in disagreement with Minkowski's data. It is to be observed that for his experiments, (7) represents the accurate statistical distribution. Moreover, $\omega \gg \pi\lambda^2$. If then the center of the line is completely absorbed and measurements are confined to its wings, $|\nu| \gg \omega \gg \pi\lambda^2$. Under this condition $I \sim \nu^{-2}$ on the blue side, $I \sim \nu^{-\frac{3}{2}}$ on the red side of the line, as was found.

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[14] A theory pertaining to these effects has been given by Fermi, Nuovo Cimento **11**, 157 (1934).

[15] R. Minkowski, Zeits. f. Physik **93**, 731 (1935).

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NOVEMBER 1, 1935 PHYSICAL REVIEW VOLUME 48

# The Effect of Crystalline Fields on the Magnetic Susceptibilities of $Sm^{+++}$ and $Eu^{+++}$, and the Heat Capacity of $Sm^{+++}$

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(Received August 17, 1935)

The temperature variation of the paramagnetic susceptibility of $Sm^{+++}$ is calculated on the assumption that the ion is subject to a crystalline field which can be represented by the potential

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

the cubic portion of this potential predominant. The susceptibility is decreased by about 25 percent with respect to that of the free ion at 74°K when the cubic potential is so chosen as to give a separation of the $J = 5/2$ levels of about 200 cm$^{-1}$ which is of the order indicated by Spedding's work on the absorption spectrum of samarium compounds. The theoretical values of the susceptibility are then in satisfactory agreement with the experimental data of Freed over a temperature range from 74°K to room temperature. The rhombic portion of the field separates the lowest excited level into two but the contribution to the susceptibility is negligible if the rhombic separation is small compared with the cubic separation. In striking contrast with $Sm^{+++}$, Eu behaves like the free ion even in the presence of a crystalline field. The contribution to the heat capacity of $Sm^{+++}$ at various temperatures due to the excited levels is computed. When the levels which give good agreement with susceptibility data are used, the general shape of the curve is the same as that obtained experimentally by Ahlberg and Freed but the theoretical values are consistently lower than the experimental values.

## THE EFFECT OF CRYSTALLINE FIELDS ON $Sm^{+++}$

### Introduction

Van Vleck[1] has pointed out in his treatment of the paramagnetic susceptibilities in the rare earth ions that Sm[2] and Eu are anomalous in that some of the consecutive multiplet intervals are only of the order of $kT$ even though the overall multiplet widths are large. This makes it necessary to consider the populations of levels other than the ground state and also second order Zeeman terms. The theoretical values thus calculated were shown in a previous paper[3] to give good agreement with experimental data on liquids and solids over a wide temperature range even though the theory is for the free ion. This theory can be applied only when the distortion by interatomic forces is negligible, that is, the energy to "turn over" an ion against interatomic

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[1] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Chapter IX.

[2] Here as well as throughout the rest of the paper, the three plus signs are omitted. Whenever the chemical symbol Sm or Eu appears, it stands for the triply charged samarium or europium ion.

[3] A. Frank, Phys. Rev. **39**, 119 (1932).

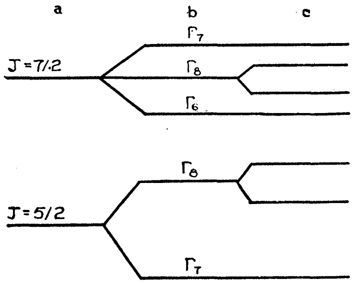

FIG. 1. The energy levels, $J=5/2$, $7/2$, of the $^6H$ configuration: (a) for the free ion and (b) in the presence of a field of cubic symmetry. The addition of a rhombic field splits the levels further as in *c*.

forces must be small compared with $kT$. It is not surprising, therefore, that the calculated values deviate considerably from the experimental data on liquid and solid compounds of samarium at low temperatures. The deviation becomes apparent at 150°K and increases as the temperature decreases.

The calculations are extended in this paper to take into account the interatomic forces for Sm and thus extend the data to lower temperatures than in the preceding article. Since the type of ionic field is unknown, the general procedure used by Penney and Schlapp[4] for other rare earths is followed, that is, we assume crystalline fields of simple symmetries and determine which types give good agreement with experimental data. The effect of such fields is to remove the degeneracy in the energy levels which exists when the intra-atomic spin-orbit interaction alone is considered. A type of field used successfully for the hydrated sulphates of other rare earths is one represented by a potential

$$V=D\sum_i(x_i^4+y_i^4+z_i^4),$$

in which the summation is taken over all of the electrons in the incomplete shell of the ion and the values of $D$ are assumed positive. The significance of the sign of $D$ has been discussed by Gorter,[5] the positive sign in the case of the rare earth salts suggesting an octahedral arrangement of the 6 oxygen atoms surrounding the metal ion.

Bethe[6] has shown that a field of cubic symmetry breaks up the $J=5/2$ state into two levels, corresponding in his notation to the irreducible representations $\Gamma_7$ and $\Gamma_8$ of the cubic group which have twofold and fourfold degeneracy, respectively. An interatomic field of rhombic symmetry splits $\Gamma_8$ further into two doubly degenerate levels. There remains the Kramers degeneracy, always present in systems with an odd number of electrons, which is removed only by a magnetic field. For the $J=5/2$ state of Sm, whose multiplet type is $^6H$, the level $\Gamma_8$ is of higher energy than $\Gamma_7$. Similarly, $J=7/2$ breaks up into three levels corresponding to $\Gamma_6$, $\Gamma_7$ and $\Gamma_8$, the fourfold degenerate level $\Gamma_8$ lying between the other two which are doubly degenerate. The $J=5/2$, $7/2$ levels of the $^6H$ configuration in the presence of crystalline fields are shown diagrammatically in Fig. 1.

An added interest in this problem arises from the experiments of Spedding,[7] who has studied the absorption spectrum of the samarium ion in solids. His work indicates an appreciable splitting of the normal state of Sm such as one would obtain with a crystalline field. However Spedding gives the separation of the normal state into four levels with a possible fifth, whereas, if the method of crystalline potentials is applicable, it is impossible to obtain more than three. Some of Spedding's observed levels fit the susceptibility data very satisfactorily. Van Vleck has suggested that the additional levels of Spedding may possibly be vibrational effects.[8]

## The Hamiltonian matrix with a cubic crystalline potential

The complete Hamiltonian function is given by

$$\mathcal{H}=A(\mathbf{L}\cdot\mathbf{S})+D\sum_i(x_i^4+y_i^4+z_i^4)+(L_z+2S_z)H\beta$$

where $z$ is taken as the direction of the applied

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[4] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932).

[5] C. J. Gorter, Phys. Rev. **42**, 437 (1932).

[6] H. Bethe, Ann. d. Physik **3**, 133 (1929).

[7] F. H. Spedding, Phys. Rev. **46**, 975 (1934).

[8] Spedding (J. Am. Chem. Soc. **54**, 2593 (1932)) has imputed some of his extra levels to "electronic isomers," thereby attributing some of the states to electronic configurations other than 4*f*. However, such an idea appears at variance with the whole Hund scheme of the magnetic susceptibilities of the rare earths, notably its success in Pr and Nd when amplified by crystalline potentials in the Penney–Schlapp fashion. Also it is doubtful whether the existence of electronic isomers would be compatible with the chemical near-identity of the various rare earths. Even if Spedding's electronic isomer model were accepted, his attempted calculation of the magnetic susceptibility of Sm by this model would be in error. Among the mistakes we may mention the fact that, if the orbital magnetic moment were quenched, the statistical weight of the upper state would be 2 and not 18.

| | 1 | 6 | 7 |
|---|---|---|---|
| 1 | $W_{5/2}-348Q-G/7$ | $1560(6)^{\frac{1}{2}}Q/11$<br>$+5(6)^{\frac{1}{2}}G/14$ | $(210)^{\frac{1}{2}}G/14$ |
| 6 | $1560(6)^{\frac{1}{2}}Q/11$<br>$+5(6)^{\frac{1}{2}}G/14$ | $W_{7/2}-17{,}048Q/33$<br>$+286G/189$<br>$+1183G^2/810F$ | $-52(35)^{\frac{1}{2}}G/189$ |
| 7 | $(210)^{\frac{1}{2}}G/14$ | $-52(35)^{\frac{1}{2}}G/189$ | $W_{7/2}-19{,}544Q/33$<br>$+26G/27$<br>$+91G^2/54F$ |

FIG. 2. Cubic factor of the secular determinant $\mathcal{H}'$. Numbers designating rows and columns correspond to subscripts on the wave functions $\psi_n'$.

| | 2 | 5 | 3 | 4 |
|---|---|---|---|---|
| 2 | $W_{5/2}-348Q$<br>$-11G/21$ | $1560(6)^{\frac{1}{2}}Q/11$<br>$-5(6)^{\frac{1}{2}}G/14$ | $4(5)^{\frac{1}{2}}G/21$ | $-5(2)^{\frac{1}{2}}G/14$ |
| 5 | $1560(6)^{\frac{1}{2}}Q/11$<br>$-5(6)^{\frac{1}{2}}G/14$ | $W_{7/2}-17{,}048Q/33$<br>$+26G/63$<br>$+1547G^2/810F$ | $-(30)^{\frac{1}{2}}G/7$ | $-52(3)^{\frac{1}{2}}G/63$ |
| 3 | $4(5)^{\frac{1}{2}}G/21$ | $-(30)^{\frac{1}{2}}G/7$ | $W_{5/2}-816Q$<br>$+5G/21$ | $-1560(10)^{\frac{1}{2}}Q/11$<br>$+2(10)^{\frac{1}{2}}G/7$ |
| 4 | $-5(2)^{\frac{1}{2}}G/14$ | $-52(3)^{\frac{1}{2}}G/63$ | $-1560(10)^{\frac{1}{2}}Q/11$<br>$+2(10)^{\frac{1}{2}}G/7$ | $W_{7/2}-12{,}888Q/33$<br>$-26G/21$<br>$+91G^2/54F$ |

FIG. 3. Quartic factor of the secular determinant $\mathcal{H}'$.

magnetic field and $\beta$ is the Bohr magneton $eh/4\pi mc$. $A(\mathbf{L}\cdot\mathbf{S})$ is the spin-orbit interaction which is diagonal in $J$ (and independent of $M$) since we assume that the crystalline field does not destroy the Russell-Saunders coupling. The eigenvalues of $A(\mathbf{L}\cdot\mathbf{S})$ will be referred to as $W_J$.

$(L_z+2S_z)H\beta$ is the contribution to the energy due to the presence of the magnetic field. This is regarded as a small perturbation in calculating the susceptibility, inasmuch as the magnetic separation is small compared with $kT$. As has been emphasized previously,[3] the calculations for Sm and Eu differ from those of the rest of the rare earth group in that the separation between the lowest multiplet levels is comparable with $kT$. It is therefore necessary to take into account the off-diagonal elements of the energy due to the magnetic field, formulae for which are given elsewhere.[9] In the complete secular determinant only the levels $J=5/2$ and $J=7/2$ are considered since, at low temperatures higher levels are not appreciably occupied, whereas at high temperatures the interaction between ions in the crystal, accounted for by the cubic potential, is not important. However, the interaction between $J=7/2$ and $J=9/2$ is not neglected insofar as the magnetic moment is concerned. This contribution to the magnetic moment is taken care of by adding to the diagonal elements of $J=7/2$ the second-order perturbation term $[(L_z+2S_z)(J,M;J+1,M)]^2/(W_J-W_{J+1})$ with $J=7/2$.

General expressions for the elements of the cubic field potential are given by Schlapp and Penney[10] in either the $J$, $M$ or $M_L$, $M_S$ systems of representation and so need not be repeated here. These, however, do not include the elements off-diagonal in $J$ which may be obtained by expanding the wave functions in the form

$$\psi_{J,\,M}=\sum_{M_L} S^{L,\,S}_{J,\,M,\,M_L}\;\psi^{L,\,S}_{M_L,\,M-M_L}.$$

The coefficients in the expansion are given by Wigner.[11] For the multiplet type ${}^6H$, the elements

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[9] J. H. Van Vleck, reference 1, p. 167.

[10] R. Schlapp and W. G. Penney, Phys. Rev. **42**, 666 (1932). See also reference 4.

[11] E. Wigner, *Gruppentheorie*, p. 206.

of $V=D\sum_i(x_i^4+y_i^4+z_i^4)$ not diagonal in $J$ are, for $J=5/2$:

$$\begin{aligned} V(J,\,M;\,J+1,\,M)=V(J+1,\,M;\,J,\,M)\qquad&\\ =-1560\,(5)^{\frac{1}{2}}\,Q/11\qquad&(M=\pm5/2)\\ =-2080\,(3)^{\frac{1}{2}}\,Q/11\qquad&(M=\pm3/2)\\ =\quad 780\,(10)^{\frac{1}{2}}Q/11\qquad&(M=\pm1/2)\end{aligned}$$

$$\begin{aligned} V(J,\,M;\,J+1,\,M\mp4)=V(J+1,\,\mathrm{M}\mp4;\,J,\,M)\qquad&\\ =-520\,(15)^{\frac{1}{2}}Q/11\qquad&(M=\pm5/2)\\ =\ 3120\qquad Q/11\qquad&(M=\pm3/2)\\ =-780\,(14)^{\frac{1}{2}}Q/11\qquad&(M=\pm1/2)\end{aligned}$$

with $Q=q'D/c$. $D$ is the cubic field constant, $q'$ is the ratio of the matrix elements calculated for a system of $n$ electrons to those for a one electron system, and $c$ is a constant computed for a one electron system. The constant $q'/c$ is the same as the absolute value of the constant $q$ used by Penney and Schlapp.[4] By use of spur relations as explained by Penney and Schlapp, $q'/c$ is determined to be $+503I/165$ with $I=\int_0^\infty r^6R^2(r)dr$. $R(r)$ is the radial wave function for one of the equivalent electrons. The positive value thus obtained for $q'/c$ requires $\Gamma_7$ to be of lower energy than $\Gamma_8$ for $J=5/2$ for the type of cubic field we have assumed in which $D$ is positive (see Fig. 1).

If the elements off-diagonal in $J$ are neglected, the secular determinant factors, no factor being of higher order than two. The complete determinant is therefore simplified by transforming to a system of representation which diagonalizes those terms of the cubic field potential already diagonal in $J$. The following transformation of the original wave functions ($\psi_{J,\,M}$) accomplishes this simplification:

$$\begin{aligned}
\psi_{\pm1}'&=\psi_{5/2,\,\pm1/2},\\
\psi_{\pm2}'&=(5/6)^{\frac{1}{2}}\psi_{5/2,\,\pm3/2}+(1/6)^{\frac{1}{2}}\psi_{5/2,\,\mp5/2},\\
\psi_{\pm3}'&=(5/6)^{\frac{1}{2}}\psi_{5/2,\,\mp5/2}-(1/6)^{\frac{1}{2}}\psi_{5/2,\,\pm3/2},\\
\psi_{\pm4}'&=(3/4)^{\frac{1}{2}}\psi_{7/2,\,\mp5/2}+(1/2)\psi_{7/2,\,\pm3/2},\\
\psi_{\pm5}'&=(3/4)^{\frac{1}{2}}\psi_{7/2,\,\mp5/2}-(1/2)\psi_{7/2,\,\pm3/2},\\
\psi_{\pm6}'&=(5/12)^{\frac{1}{2}}\psi_{7/2,\,\pm7/2}+(7/12)^{\frac{1}{2}}\psi_{7/2,\,\mp1/2},\\
\psi_{\pm7}'&=(5/12)^{\frac{1}{2}}\psi_{7/2,\,\mp1/2}-(7/12)^{\frac{1}{2}}\psi_{7/2,\,\pm7/2}.
\end{aligned}$$

Figs. 2 and 3 give the secular determinant $\mathcal{H}'$ in this new system of representation, factored into two identical quartics and two identical cubics with $F$ substituted for $(W_{7/2}-W_{9/2})$, and $G$ for $H\beta$.

TABLE I. *Effective Bohr magneton numbers for Sm.*

| $T$°K | $\mu_{\mathrm{eff}}$ (THEORY) $\nu=0$ (cm)$^{-1}$ (FREE ION) | 173.6 (cm)$^{-1}$ | 207 cm$^{-1}$ | $\mu_{\mathrm{eff}}$ (EXP.) FREED[12] |
|---|---|---|---|---|
| 74 | 1.06 | .94 | .91 | .91 |
| 85 | 1.09 | .99 | .97 | .96 |
| 112 | 1.16 | 1.11 | 1.09 | 1.08 |
| 170 | 1.29 | 1.28 | 1.27 | 1.26 |
| 205 | 1.37 | 1.37 | 1.36 | 1.35 |
| 240 | 1.44 | 1.44 | 1.44 | 1.44 |
| 293 | 1.55 | 1.56 | 1.56 | 1.57 |

The terms off the diagonal which depend on the cubic field occur in such a way as to require the solution of nothing more complicated than a quadratic to completely diagonalize them. Such a transformation, however, presents numerical difficulties because of the scrambling of the $J=5/2$ and $J=7/2$ terms. It would be possible to carry out the calculation in general terms by expanding the radicals which occur in the transformation matrix in terms of $Q/(W_J-W_{J+1})$. It is less laborious to make this second transformation by the substitution of numerical values for $W_J$ and $Q$, until by trial and error a value of $Q$ is found which gives results in agreement with experimental data. The values substituted for $W_J$ are the multiplet energies used in the previous work on Sm, with the screening constant $\sigma$ taken as 33.

Energy values are obtained to second powers in the magnetic field $H$ by applying perturbation theory to the matrix $\mathcal{H}''$ which results from the second transformation and which is therefore diagonal except for linear terms in $H$. Thus

$$W_n=\mathcal{H}''(n;\,n)+\sum_{n'}\frac{[\mathcal{H}''(n;\,n')]^2}{W^0(n;\,n)-W^0(n';\,n')},$$

where $W^0(n;\,n)$ is that part of $\mathcal{H}''(n;\,n)$ independent of the magnetic field.

## Comparison of computed and experimental susceptibilities

Several sets of energy levels $W_n$ corresponding to several choices of the constant $Q$ were used and the molar susceptibility ($\chi$) readily calculated from

$$\chi=\frac{NkT}{H}\frac{d\log Z}{dH},$$

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[12] S. Freed, J. Am. Chem. Soc. 52, 2702 (1930).

where $Z$ is the partition function

$$Z=\sum_n e^{-W_n/kT}.$$

Table I gives computed and experimental values at various temperatures of the effective Bohr magneton number defined as

$$\mu_{\mathrm{eff}}=[3kT\chi/N\beta^2]^{\frac{1}{2}}.$$

The values of $\nu$ referred to in the table are values of the separation of the $J=5/2$ level due to the cubic field corresponding to different choices of the constant $Q$. It is evident from the table that satisfactory agreement is obtained when the splitting of the $J=5/2$ level due to the cubic field is in the neighborhood of 200 $\mathrm{cm}^{-1}$.

Experimental values of $\mu_{\mathrm{eff}}$ at room temperature reported by other observers are

| | | |
|---|---|---|
| 1.58 | (anh. sul.) | Cabrera and Duperier[13] |
| 1.55 | (hyd. sul.) | Selwood[14] |
| 1.66 | (hyd. sul.) | Rodden.[15] |

The high effective magneton number given by Rodden would be in satisfactory agreement with the theory if the screening constant were taken as 34 instead of 33. Experimental values for the oxides of samarium are not included since it is not expected that the same type of crystalline field applies to both oxides and sulphates.[16]

### The effect of adding a small rhombic potential to the crystalline field

Spedding[7] has reported excited levels at 160 $\mathrm{cm}^{-1}$, 188 $\mathrm{cm}^{-1}$, 225 $\mathrm{cm}^{-1}$, and possibly one at 245 $\mathrm{cm}^{-1}$ from the absorption spectrum of $\mathrm{Sm_2(SO_4)_3\cdot 8H_2O}$. The values of $\nu$ chosen for Table I are approximately the mean of 160 $\mathrm{cm}^{-1}$ and 188 $\mathrm{cm}^{-1}$, and the mean of 188 $\mathrm{cm}^{-1}$ and 225 $\mathrm{cm}^{-1}$. An interatomic field of rhombic symmetry will remove the degeneracy in the upper $J=5/2$ level but will leave the center of gravity unchanged. The calculation which follows shows that the inclusion of a rhombic field which will separate this level into two of those reported by Spedding will not destroy the good agreement with experimental data insofar as the susceptibility is concerned.

The rhombic field can be represented by the potential

$$\sum_i [Ax_i^2+By_i^2-(A+B)z_i^2],$$

the matrix elements of which are given by Schlapp and Penney.[10] If this rhombic field is assumed to be a small perturbation, it is sufficient to consider the effect only on the lowest levels of Sm. In the Hamiltonian matrix which results from the first transformation of the wave functions, new elements $\mathcal{H}'(n;\,n')=\mathcal{H}'(n';\,n)$ are added as follows:

$$\begin{aligned}
&\mathcal{H}'(1;\,1)=-\mathcal{H}'(2:2)=4a(A+B),\\
&\mathcal{H}'(1;\,2)=4a(A-B)/(3)^{\frac{1}{2}},\\
&\mathcal{H}'(1;\,3)=-(5)^{\frac{1}{2}}a(A+B),\\
&\mathcal{H}'(2;\,3)=(5)^{\frac{1}{2}}a(A-B)/(3)^{\frac{1}{2}}
\end{aligned}$$

with $a=a'/b'$, where $a'$ is the ratio of the matrix elements calculated for a system of $n$ electrons to those for a one electron system, and $b'$ is the constant calculated for a one electron system.

The addition of the rhombic terms to the complete secular determinant complicates it considerably. For example, the addition of the elements $\mathcal{H}'(1;\,2)$ and $\mathcal{H}'(1;\,3)$ spoils the factorization into quartics and cubics as given by Figs. 2 and 3. However, if we assume the energy ($R$) due to the rhombic field small compared with $kT$ and also small compared with the separation ($h\nu$) due to the cubic field, it is possible to expand the susceptibility in terms of $R/kT$ and $R/h\nu$. Then, by using spur relations, the contribution due to the rhombic field can be determined without solving the secular determinant which includes these terms. A general expression for this expansion in terms of spurs is given by Serber.[17]

Since the matrix elements of the magnetic moment were originally given corresponding to the application of the magnetic field along the $z$ axis, it is necessary to determine the magnetic moment along the $x$ and $y$ axes in order to compute the average susceptibility. This can be done most conveniently by a cyclic permutation of the rhombic parameters, $A$, $B$, and $-(A+B)$.

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[13] Experimental values on anhydrous sulphates of Sm and Eu were communicated by Professor Cabrera to Professor Van Vleck. Earlier work of Cabrera and Duperier on hydrous sulphates of Sm and Eu may be found in Compte rendus **188**, 1640 (1929).

[14] P. W. Selwood, J. Am. Chem. Soc. **56**, 2392 (1934).

[15] C. J. Rodden, J. Am. Chem. Soc. **56**, 648 (1934).

[16] Experimental values of the susceptibility of $\mathrm{Sm_2O_3}$ of various observers are tabulated by C. Wiersma and B. H. Schultz, Physica **13**, 171 (1933), P. W. Selwood, reference 14, and A. Frank, reference 2.

[17] R. Serber, Phys. Rev. **43**, 1011 (1933).

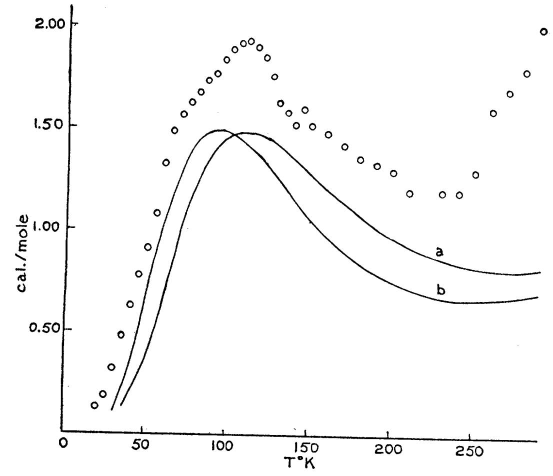

FIG. 4. Variation of electronic heat capacity of $Sm^{+++}$ with temperature. Solid lines show theoretical values using levels at (a) 187 and 225 $cm^{-1}$, (b) 160 and 187 $cm^{-1}$. Circles designate experimental values of Ahlberg and Freed.

The terms in the expansion are symmetric in $A$, $B$, and $-(A+B)$ and therefore those which are of the first order in the rhombic field energy average to zero. The average contribution to the susceptibility is proportional to the square of the separation due to the rhombic field, to as good an approximation as is needed.

The computations show that the addition of the rhombic splitting has little effect on the susceptibility, as long as it is small compared with the cubic portion of the field. For example, with $\nu=192$ $cm^{-1}$, a rhombic separation of 65 $cm^{-1}$ (giving Spedding's levels 160 and 225 $cm^{-1}$) lowers $\mu_{\text{eff}}$ by only 0.8 percent at 74°K, the change in $\mu_{\text{eff}}$ decreasing with increasing temperatures. For smaller rhombic separations, the decrease in $\mu_{\text{eff}}$ rapidly becomes less so that, with $\nu=174$ $cm^{-1}$, the effect of a rhombic separation of 25 $cm^{-1}$ (giving Spedding's levels 160 and 187 $cm^{-1}$) is negligible. Thus the important factor is the mean of the excited levels and any two of the levels reported by Spedding give values for the susceptibility in satisfactory agreement with the experimental data available. Therefore we may conclude that the samarium ion in a solid such as $Sm_2(SO_4)_3 \cdot 8H_2O$ is probably in a crystalline field, predominantly of cubic symmetry such that the separation of the $J=5/2$ level is in the neighborhood of 200 $cm^{-1}$.

TABLE II. *Effective Bohr magneton numbers for Eu.*

| | $\mu_{\text{eff}}$ (THEORY)[2] | | | $\mu_{\text{eff}}$ (EXPERIMENT) | | |
|---|---|---|---|---|---|---|
| $T$°K | $\sigma=33$ | $\sigma=34$ | SELWOOD[18] | HUGHES & PEARCE[19] (hyd. sul.) | CABRERA & DUPERIER[13] (hyd. sul.) | (anh. sul.) |
| 83 | 2.18 | 2.33 | 2.06 | | | |
| 153 | 2.84 | 2.97 | 2.73 | | | |
| 223 | 3.18 | 3.29 | 3.14 | | | |
| 293 | 3.40 | 3.51 | 3.41 | 3.63 | 3.61 | 3.53 |
| 343 | 3.53 | 3.63 | 3.58 | | | |
| 400 | 3.65 | 3.75 | | | | 3.75 |

### Temperature variation of the heat capacity in Sm

The contribution of the multiplet levels to the heat capacity of Sm at various temperatures is given in a previous paper but these values are increased considerably by the assumption of a crystalline field which splits the lowest multiplet level. The solid lines of Fig. 4 show the theoretical curves for the temperature variation of the heat capacity. Curves for other combinations of levels which give good agreement with the susceptibility data lie close to those given on the graph. The lack of good agreement with the absolute values found experimentally by Ahlberg and Freed[20] is not surprising. These experimental values represent the difference between the heat capacities of $\frac{1}{2}[Sm_2(SO_4)_3 \cdot 8H_2O]$ and $\frac{1}{2}[Gd_2(SO_4)_3 \cdot 8H_2O]$. Since these are large quantities relative to their difference, possibly the error in the difference may be considerable. Moreover additional levels as reported by Spedding would contribute to the heat capacity.

## EFFECT OF CRYSTALLINE FIELDS IN EU

### Experimental data

Since the previous work on the theoretical susceptibility for the free europium ion,[2] several experimenters have published values of the susceptibilities of europium compounds. Table II lists the data on sulphates as one may expect these values to give better agreement with the theory for the free ion than values obtained from the oxides, since the latter are firmer chemical compounds. The fact that Selwood's values at temperatures below room temperature are lower

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[18] P. W. Selwood, J. Am. Chem. Soc. 55, 4869 (1933).

[19] Hughes and Pearce, J. Am. Chem. Soc. 55, 3277 (1933). It is not stated in this paper whether diamagnetic corrections had been made.

[20] J. Ahlberg and S. Freed, J. Am. Chem. Soc. 57, 431 (1935).

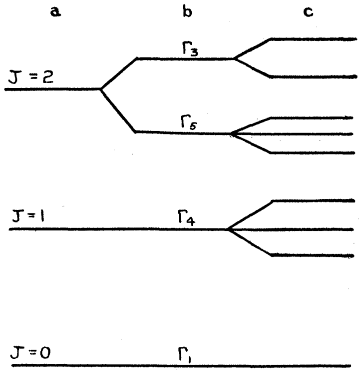

FIG. 5. The energy levels, $J=0$, 1, 2, of the $^7F$ configuration: (a) for the free ion and (b) in the presence of a field of cubic symmetry. The addition of a rhombic field splits the levels further as in *c*.

than the theoretical values suggests the possibility that the susceptibility is lowered by a crystalline field as in the case of Sm. However, calculations similar to those for Sm show that the presence of fields of cubic and rhombic symmetry has very little effect upon Eu.

## Effect of crystalline fields on the energy values and the susceptibility

It is not surprising that the effect of a crystalline field of cubic symmetry is less for the europium ion than for samarium because the lowest state ($J=0$) is nondegenerate and the degeneracy in the $J=1$ level is not removed by the cubic field. The analysis of Bethe shows that the $J=2$ level separates into two levels corresponding to the irreducible representations $\Gamma_3$ and $\Gamma_5$. Furthermore, since $J=2$ and $J=1$ belong to different representations of the cubic group, there are no matrix elements of the cubic field between them. For Eu, whose multiplet type is $^7F$, the doubly degenerate $\Gamma_3$ level is of higher energy than the triply degenerate $\Gamma_5$ level. A diagram of these levels is given in Fig. 5.

It is sufficient for the purpose of this calculation to consider the effect of a cubic field which partially removes the degeneracy in the $J=2$ level, and a rhombic field which completely removes the threefold degeneracy in the $J=1$ level. If the effect of the rhombic matrix elements between $J=1$ and $J=2$ and of cubic elements between $J=2$ and $J=3$ are neglected, the secular determinant is readily diagonalized in all but the magnetic terms, and their contribution to the energy may be obtained by perturbation theory.

With the rhombic field absent and the cubic separation equal to 200 cm$^{-1}$, the effective Bohr magneton number is smaller than that for the free ion by 1 percent at room temperature when the screening constant is taken as 34. The change in $\mu_{\text{eff}}$ is less when the screening constant is taken as 33. At low temperatures the change is negligible since only the normal state has an appreciable population and the normal state is not affected by the cubic field. Moreover a cubic separation as great as 200 cm$^{-1}$ is improbable in Eu. In terms of constants defined previously in connection with the discussion of the cubic field in Sm, the energy of separation of the $J=2$ level due to the cubic field is $440Q/7=260ID/63$. If we assume the integral $I$ to be nearly the same in both cases, the value of $D$ necessary to separate the $J=2$ level of Eu by 200 cm$^{-1}$ must be about 350 times the value to separate the $J=5/2$ level of Sm by the same amount. And since even the improbable separation of 200 cm$^{-1}$ produces little change in the effective magneton number, Eu may be considered gas-like in the presence of a cubic field, a result which one should expect from the group theory analysis since the cubic field has no effect on the lowest two levels of Eu.

The average contribution due to the rhombic field may be determined by expanding the expression for the susceptibility if we assume the rhombic energies small compared with $kT$ and small compared with the multiplet energies. The rhombic terms increase $\mu_{\text{eff}}$ by less than 1 percent at 83°K if the maximum separation introduced by the rhombic field is 100 cm$^{-1}$. The change due to the rhombic field is less at higher temperatures. Thus the effect of crystalline fields may be considered of little importance in the case of Eu.

In conclusion I wish to express my gratitude to Professor J. H. Van Vleck under whose guidance this work was done.