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Energy Levels for Rare Earth Ions Subject Both to Exchange and Crystalline Fields

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The term splitting has been calculated for the lowest lying J state of the rare earth ions samarium through through ytterbium for the case in which the ions are simultaneously subjected to exchange and crystalline fields of arbitrary relative magnitude. The crystalline field is taken to be cubic and as representing the potential of eight negative ions situated at the corners of a cube. The calculation is carried out for the magnetic axis in the two major (local) crystalline directions, [100] and [111]. The relevance of these calculations to the rare earth iron garnets is discussed.

INTRODUCTION

THE subject of term splitting of ions in crystals has long been of interest to physicists, and the increased attention paid it in recent years has been stimulated by the invention of the solid-state maser. Group-theoretical techniques built upon the pioneer work of Bethe[1] enable one to predict the character of the term splitting when only the symmetry properties of the perturbing fields are known; computational procedures have been developed by Van Vleck[2] and coworkers and Elliott and Stevens[3] for calculating the energy matrix elements arising from the perturbing fields. The problem of calculating the actual splitting in some simple cases then reduces to diagonalizing a matrix of finite but awkwardly large dimension.

In most physical systems hitherto of interest, the electric-field (Stark) splittings of the ions involved were orders of magnitude greater than the magnetic splittings, so the magnetic splittings of either dipolar or exchange origin have usually been calculated as additional small perturbations upon Stark-determined states. In a recently discovered crystal system of great physical interest—the ferrimagnetic rare earth iron garnets—the magnetic splittings are equivalent in size to the electric splittings; hence one is led to consider the diagonalizing of energy matrices containing crystalline field and magnetic exchange elements of equivalent size.

CHARACTERISTICS OF THE RARE EARTH IONS IN CRYSTALS

The intriguing features of the rare earth ions are mostly associated with the partially filled and deeply buried $4f$ shells characteristic of these elements. The neutral atoms have an electronic configuration which can be written in the conventional notation as

$$(1s)^2(2s)^2\cdots(4f)^x(5s)^2(5p)^6 5d(6s)^2,$$

where x ranges from 0 to 14. The rare earths commonly enter ionic crystals in a trivalent state, having lost the one $5d$ and two $6s$ electrons. All net angular momentum then resides in the unfilled $4f$ shell, which is shielded from external fields by the eight $5s$ and $5p$ electrons. The shielding is sufficiently effective that the crystalline Stark splitting of the free ion terms totals only hundreds of reciprocal centimeters, as contrasted with the splitting of thousands of reciprocal centimeters typical, say, of the transition elements. The Stark splitting is an inverse function of x, the number of $4f$ electrons present, and diminishes from about 600 cm^{-1} for Ce^{+++} ($x=1$) to about 100 cm^{-1} for Yb^{+++}($x=13$). The spin-orbit interaction is sufficiently strong (except for Eu and Sm) that it separates the terms of different J by thousands of cm^{-1}; therefore, even in the crystal, J usually remains a "good" quantum number. The total term splitting of some 10^2 cm^{-1} is further divided among the $2J+1$ levels within a term, which gives rise to individual splittings on the order of tens of cm^{-1} and explains why at room temperatures ($kT=200$ cm^{-1}) the rare earth ions exhibit almost free-ion magnetic susceptibility.

The rare earth ions with $x>5$ are of appropriate radius to enter the rare earth iron garnets ($3\text{R}_2\text{O}_3\cdot5\text{Fe}_2\text{O}_3$).[4] In this crystal the ions are not only acted upon by crystalline electric fields, but they also participate in an exchange interaction with the iron ions involving energies of about 25 cm^{-1} per unbalanced $4f$ electron spin. Since as many as seven unbalanced spins can occur, the term splitting due to exchange is, in general, of approximately the same magnitude as the Stark splitting. The following calculations were undertaken to examine the behavior of the energy levels of such a system.

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[1] H. A. Bethe, Ann. Physik **3**, 133 (1929).

[2] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932); Phys. Rev. **41**, 208 (1932); W. G. Penney and R. Schlapp, Phys. Rev. **41**, 195 (1932); R. Schlapp and W. G. Penney, Phys. Rev. **42**, 666 (1932); W. G. Penney and G. J. Kynch, Proc. Roy. Soc. (London) **A170**, 112 (1939); G. J. Kynch, Trans. Faraday Soc. **33**, 1402 (1937).

[3] R. J. Elliott and K. W. H. Stevens, Proc. Phys. Soc. (London) **A64**, 205 (1951); **A64**, 932 (1951); **A65**, 370 (1952). K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952); R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A215**, 437 (1952).

[4] F. Bertaut and F. Forrat, Compt. rend. **242**, 382 (1956); S. Geller and M. A. Gilleo, Acta. Cryst. **10**, 239 (1957); Aleonard, Barbier, and Pauthenet, Compt. rend. **242**, 2531 (1956); R. Pauthenet, Compt. rend. **242**, 1859 (1956); **243**, 1499 (1956); **243**, 1737 (1956). R. Pauthenet, thesis, University of Grenoble, 1958 (unpublished).

FORMULATION OF THE PROBLEM

We will take the perturbing potentials which the free ion encounters when placed in the crystal as

$$\begin{aligned} H_c &= H(\text{Stark}) + H(\text{exchange}) \\ &= V(\text{crystal}) + 2A \textstyle\sum_{ij} \mathbf{s}_{1i} \cdot \mathbf{s}_{2j}, \end{aligned} \tag{1}$$

where V(crystal) is the electric potential generated by nearest neighbors, electrons labeled with subscript 1 reside on the perturbed ion, electrons with subscript 2 reside on the exchange-coupled neighbors, and A is the exchange energy involved. We discuss now the explicit form we shall assume for these potentials.

The rare earth ions enter the garnet lattice in a position of roughly cubic symmetry. The ion has eight (oxygen) nearest neighbors situated at the corners of a quite badly skewed cube, as illustrated in Fig. 1.[5] In the following calculation the crystalline potential will be taken to be purely cubic, and only the leading term of the potential, that which is biquadratic in the coordinates, will be included. The next higher term in the cubic potential, of sixth order in coordinates, is neglected as being (it is hoped) considerably smaller than the biquadratic terms. Effects due to all terms higher than sixth order will rigorously be zero for $4f$ electrons. The calculation must be regarded as treating a system similar to the garnet system but considerably simplified. Insofar as the cubic potential dominates the actual situation (as it very likely does), the simplified model should yield correctly the main features of the garnet system.

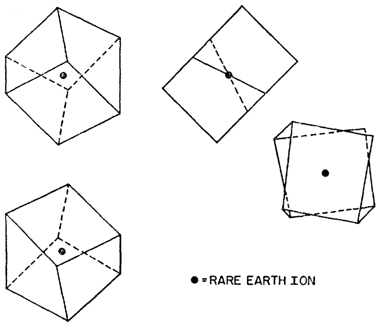

FIG. 1. Coordination polyhedron of rare earth ion in the rare earth iron garnet.[5]

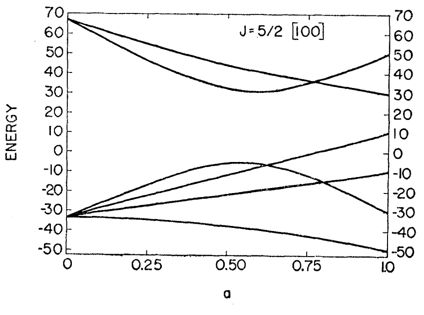

FIG. 2. Term splitting, $J=5/2$, magnetic axis in local [100] direction, arbitrary energy units.

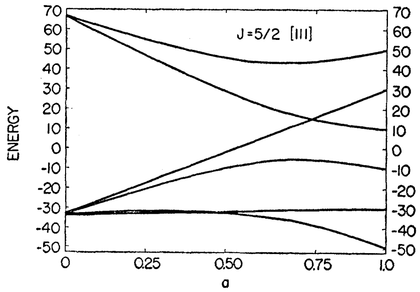

FIG. 3. Term splitting, $J=5/2$, magnetic axis in local [111] direction, arbitrary energy units.

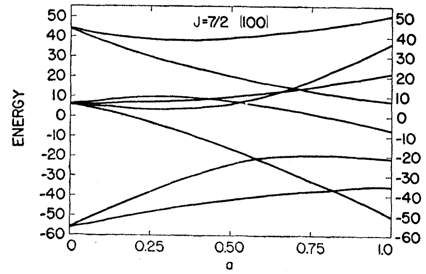

FIG. 4. Term splitting, $J=7/2$, magnetic axis in local [100] direction, arbitrary energy units.

The operator-equivalent approach of Elliott and Stevens[3] was used in obtaining an explicit form for V(crystal). The treatment regards V(crystal) as an operator acting upon the $2J+1$ dimensional space of states of fixed J. It is therefore very material to the calculation that J be a "good" quantum number. As observed earlier, the fact that configurations of different J are separated by energies from 10 to 100 times larger than the intraterm splittings (except for Eu and Sm) argues that J is indeed a good quantum number for all the rare earths with $x>7$.

The explicit form of V(crystal) involves J_z and hence depends on the direction of quantization of the free ion with respect to the crystalline axes. The energy levels are treated here for two simple cases: the magnetic axis along the local [100] and [111] directions. The local [100] and [111] directions do not correspond to the crystal [100] and [111] directions; see Fig. 1. The crystalline potentials are (following Elliott and Stevens[3])

$$\begin{aligned} V[100] &= V_0\{[35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 \\ &\quad - 6J(J+1) + 3J^2(J+1)^2] - \tfrac{5}{2}[J_+^4 + J_-^4]\}, \\ V[111] &= V_0\{-\tfrac{2}{3}[35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 \\ &\quad - 6J(J+1) + 3J^2(J+1)^2] + (10\sqrt{2}/3) \\ &\quad \times [J_z(J_+^3 + J_-^3) + (J_+^3 + J_-^3)J_z]\}. \end{aligned} \tag{2}$$

In the ensuing calculation V_0 has been chosen in a normalized fashion such that in each case the total Stark splitting is 100 scale units, and its sign has been

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[5] Figure 1 is based on data from S. Geller and M. A. Gilleo (reference 4).

taken to be that which would be given by eight negative charges at the corners of the coordination polyhedron.

The exchange energy is much simpler in form. Since the $4f$ electrons of the rare earths with $x>7$ present a case of predominantly Russell-Saunders coupling, we may assume that the separate spins assemble to form a fixed total S, accomplishing for us the summation over i of Eq. (1). In the garnet, each rare earth ion is weakly exchange-coupled to two ferric ions, which are in turn strongly exchange-coupled to other ferric ions. Below the Curie temperature the ferric ions of the crystal are bound into a state of very large effective spin $\mathcal{S}$. At low temperatures the spins of the ferric ions are substantially aligned, and taking the direction of alignment to define the z axis, we have

$$H(\text{exchange})=2n_1AS_{1z}\mathcal{S}_{2z}, \qquad (3)$$

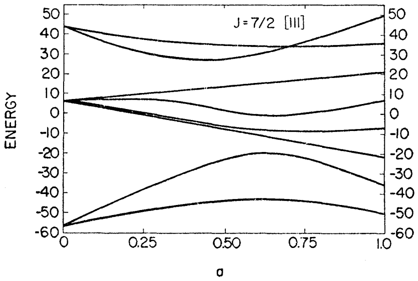

FIG. 5. Term splitting, $J=7/2$, magnetic axis in local [111] direction, arbitrary energy units.

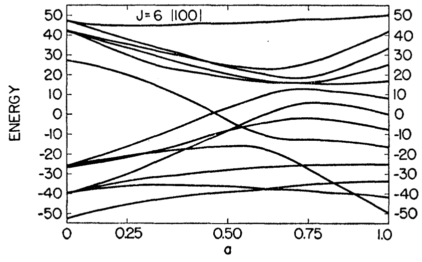

FIG. 6. Term splitting, $J=6$, magnetic axis in local [100] direction, arbitrary energy units.

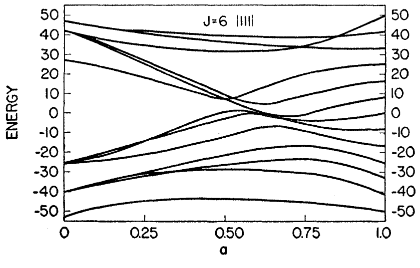

FIG. 7. Term splitting, $J=6$, magnetic axis in local [111] direction, arbitrary energy units.

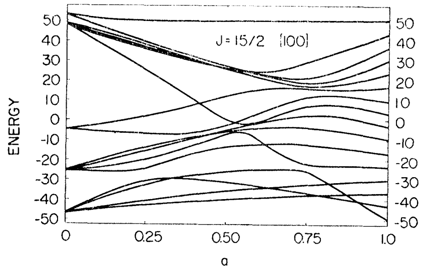

FIG. 8. Term splitting, $J=15/2$, magnetic axis in local [100] direction, arbitrary energy units.

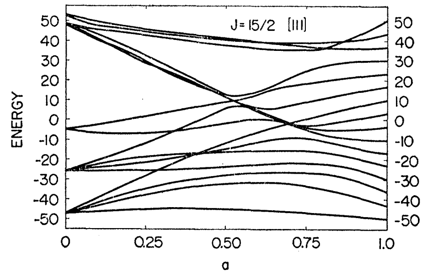

FIG. 9. Term splitting, $J=15/2$, magnetic axis in local [111] direction, arbitrary energy units.

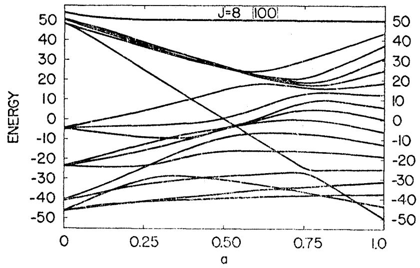

FIG. 10. Term splitting, $J=8$, magnetic axis in local [100] direction, arbitrary energy units.

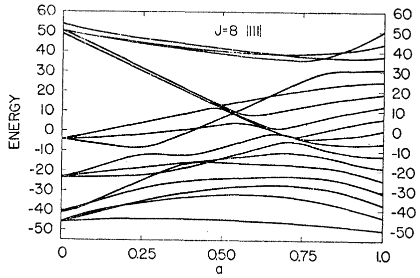

FIG. 11. Term splitting, $J=8$, magnetic axis in local [111] direction, arbitrary energy units.

where n_1 is the number of unpaired electron spins of the rare earth ion. Equation (3) assumes this simple form only because $\mathcal{S}\gg1$, a necessary condition if the transverse components of the vector dot product are to be negligible. Keeping in mind that S_1 can have a nonzero time-averaged projection only along J_1, we can redefine our energy constant and have simply

$$H(\text{exchange})=A'J_z. \qquad (4)$$

For the rare earth garnets the value of A' is approxi-

TABLE I. Rare earth ion parameters.

Ion	J	S	ΔE, cm^{-1}	ΔZ, cm^{-1}	a	ΔW/div, cm^{-1}	M_z, μ_B [111]	[100]	Free
Sm	5/2	5/2	245	125	0.34	3.7	−0.43	0.14	0.71
Eu	0	3				indeterminate			
Gd	7/2	7/2	0	175	1	1.75	7	7	7
Tb	6	3	130	150	0.54	−2.8	8.4	5.8	9
Dy	15/2	5/2	115	125	0.52	2.4	10	6.4	10
Ho	8	2	100	100	0.50	2.0	9.5	7.2	10
Er	15/2	3/2	90	75	0.45	−1.65	8.3	6.3	9
Tm	6	1	80	50	0.38	−1.3	5.9	4.2	7
Yb	7/2	1/2	70	25	0.26	0.95	2.2	2.1	4

mately known for each ion on the basis of saturation magnetization curves,[4] and in the special case of Gd^{+++} on the basis of antiferromagnetic resonance data.[6] For the purpose of calculating more generally useful curves, in the following calculation A' has also been normalized to give a total Zeeman[7] splitting of 100 scale units.

Inasmuch as we are interested in the energy term splittings as various proportions of Stark and Zeeman energies are included in the perturbing potential, the matrix elements, eigenvalues, and eigenvectors have been calculated on an IBM 704, for the perturbing Hamiltonian,

$$H_p = (1-a)H(\text{Stark}) + aH(\text{exchange}), \tag{5}$$

for values of a from 0 to 1 and for J's corresponding to the ground states of all rare earth ions entering the garnet structure. The eigenvalues for these cases are presented in graphical form in Figs. 2 through 11.[8]

INTERPRETATION AND USE OF RESULTS

The application of one of the energy-level schemes (Figs. 2 through 11) to a specific physical system requires certain prior knowledge of the system, i.e., the total Stark splitting, ΔE, and the total Zeeman splitting, ΔZ, which would be produced by the two kinds of perturbations acting separately. For the rare earth garnets, ΔE is not usually known, though the optical and infrared spectroscopy which will yield this information is under way in several laboratories. ΔE has been measured for several of the rare earths in other crystals, the fluorides, chlorides, and hydrated sulfates and nitrates.[9] Since the total splitting does not seem to be a strong function of the host crystal, one can make an estimate, good to perhaps ±50% of ΔE in the rare earth garnets. The values of ΔE listed in Table I were obtained by such an estimation process, interpolating or extrapolating from ion to ion when necessary, and must be considered to be correspondingly uncertain. There is a very good possibility that ΔE in Table I may be systematically low, if higher levels of the term splitting are absent in the references on which the estimates are based. The value of ΔZ can be obtained from the static magnetization curves of the rare earth garnets, or, for the special case of the gadolinium garnet, from the antiferromagnetic resonance data.[6] The two methods give results that are in essential agreement. The resonance measurement is probably the most accurate and leads to a ΔZ of approximately 25 cm^{-1} per unbalanced spin. The total Zeeman splitting is here taken to be linear in the unbalanced spin; the slight change in exchange energy resulting from the variation in ion size within the pertinent group of rare earths is ignored. The static magnetization data of the garnets indicate that this linear approximation is essentially valid.

Knowing ΔE and ΔZ, one can calculate a, the parameter in Figs. 2 through 11 that specifies the relative importance of Stark and Zeeman splitting:

$$a = \Delta Z/(\Delta Z + \Delta E). \tag{6}$$

The ordinate scale in energy units at any a is given by

$$\Delta W/\text{div} = (\Delta E + \Delta Z)/100. \tag{7}$$

All these parameters are listed for each ion of interest in Table I together with values of M_z of the lowest lying energy level for the magnetic axis in each of the two directions treated. M_z is calculated from the eigenvectors of the ground state, which are not tabulated explicitly in this article. Identification of the lowest lying energy level requires knowledge of which ordinate direction represents increasing energy; for a given crystal potential and J, the Stark splitting may still be of either sign, depending on the composition of the J state, and Figs. 2 through 11 could be either right side up or upsidedown. The figures have all been plotted right side up as referred to the rare earth garnet configuration on the basis of the calculations of Elliott and Stevens,[3] with the exceptions of Tb, Er, and Tm, for which the figures are inverted.

Various macroscopic magnetic characteristics of the rare earth garnets can, in principle, be calculated or estimated from a knowledge of the rare earth ion levels: saturation magnetization at low temperatures, magnetic anisotropy, effective g-factors and line widths in ferrimagnetic resonance. Some of these properties will be calculated in a subsequent article. However, it is appropriate here to point out some of the difficulties inherent in this subject for the benefit of those intending to make similar use of the individual-ion information.

First, the crystal directions of the cubic garnet unit cell do not coincide with the directions of the local

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[6] Geschwind, Walker, and Linn (to be published).

[7] All magnetic-like energies, including exchange, will be loosely termed Zeeman energies in the following discussion.

[8] Compare Fig. 4 with a similar plot in C. Kittel and J. M. Luttinger, Phys. Rev. **73**, 162 (1948).

[9] An inclusive list of references on the subject of optical spectroscopy and low-temperature susceptibility measurements of the rare earth ions would be prohibitively long. The Stark splittings in Table I were based on several sources, largely publications bearing the names Spedding, Nutting, Mookherji, Hellwege, and Dieke. A recent review article with a comprehensive relevant bibliography is W. A. Runciman, Repts. Prog. in Phys. **21**, 30 (1958).

coordination cube. The oxygen cubes occur in the unit cell in six inequivalent positions, with one local ⟨100⟩ direction of each along one of six different ⟨110⟩ directions of the unit cell. Figure 1 is drawn with the unit cell ⟨100⟩ directions used as coordinates and shows only one of the six possible local configurations.

Second, the magnetic axis in Figs. 2 through 11 is determined by the direction of M_{Fe}, not of the applied magnetic field. Since the absolute energy of the lowest-lying level is a strong function of the direction of magnetic axis (differing by 8 cm^{-1} from [100] to [111] in Dy^{+++}), there is a marked tendency for the rare earth ion to twist the polarization of the Fe ions to which it couples away from H_{external}. The macroscopic magnetic properties will have the symmetry of the unit cell, but strong distortions of M within the unit cell must be expected.

Finally, the idealizations of the local symmetry mentioned earlier are again reiterated to indicate the degree of uncertainty which must reside in any calculation of properties of the total actual system.

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Properties of Alkali Halide Crystals at Low Temperatures[*]

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Recent experimental results on low-temperature heat capacities and elastic constants of alkali halide crystals are examined for evidence of anharmonic contributions. It is concluded that if such effects are present their contribution to the characteristic temperature at 0°K is less than that of uncertainties in the experimental results.

SOME new experimental results on low-temperature properties of alkali halide crystals were recently obtained at the Rice Institute, and reported in this journal. Norwood and Briscoe[1] have measured elastic properties of KCl and KI over the temperature range 4° to 300°K, and Scales[2] has measured heat capacities of LiF and KI over the range 2° to 7°K. One aim of this work was to compare the limiting characteristic temperatures, Θ_0 and Θ(elastic), given, respectively, by calorimetric and elastic measurements as T approaches 0°K. These should be equal provided that the lattice vibrations are purely harmonic; but recent work by Ludwig[3] has suggested that a combination of zero-point energy and anharmonicity may cause differences of the order of 1%. The conclusion reached in the Rice Institute papers is that some of the experimental results may support Ludwig's theory.

It is clear that modern refinements in experimental technique are beginning to make it worth while to look for anharmonic effects in the heat capacity of crystals,[4] but in order to detect these it is important that the consequences of *harmonic* lattice theory be kept clearly in mind during the examination and interpretation of experimental results. We believe that the Rice Institute papers are open to criticism in this respect and that some of their arguments could be seriously misleading; this applies particularly to Scales's estimation of Θ_0 from his experimental results.

THE ESTIMATION OF Θ_0

Scales starts by assuming that below a temperature of the order of $\Theta_0/50$ a "true T^3 region" is reached, in which $C_v=aT^3$; in this region Θ_D would be effectively constant and equal to Θ_0. Now this assumption neglects the effect of dispersion on the lattice waves of low frequency, which in fact introduces further terms in higher powers of T into the expansion for the heat capacity. The contribution of such terms does not in general suddenly disappear at some finite temperature, as is suggested by Scales's graph of Θ_D for KI (his Fig. 6). On the contrary, Θ_D must approach a constant value asymptotically according to the expansion

$$\Theta_D=\Theta_0\{1-A(T/\Theta_0)^2+B(T/\Theta_0)^4\cdots\}; \tag{1}$$

this is equivalent to the quite general expansion for the lattice heat capacity

$$C_v=aT^3+bT^5+cT^7+\cdots. \tag{2}$$

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[*] National Research Contract No. 5395.

[1] M. H. Norwood and C. V. Briscoe, Phys. Rev. **112**, 45 (1958).

[2] W. W. Scales, Phys. Rev. **112**, 49 (1958).

[3] W. Ludwig, J. Phys. Chem. Solids **4**, 283 (1958).

[4] Flubacher, Leadbetter, and Morrison, Phil. Mag. **4**, 273 (1959).