

the assumption that the Feynman state is nearly the true excited state.

#### IV. CONCLUSIONS

We have found that expressions for the sound velocity and the chemical potential derived in a previous paper are in order-of-magnitude agreement with known results in two cases which we checked. The approximate formalism described the ground-state properties of the

many-boson system quite accurately in the case treated. Properties of the excitation spectrum were given less accurately, but reasons were given for the deviations. Two formally different expressions for the sound velocity have given the same numerical result for the case of actual liquid  $\text{He}^4$ . The results of this work show that further study of the representation of the energy spectrum of a Bose system by its density fluctuations is desirable.

## Optical Spectra of Trivalent Iron in Trigonal Fields

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The energy levels of  $\text{Fe}^{3+}$  in  $\text{Al}_2\text{O}_3$  have been calculated. The eigenvalues were obtained by first calculating the matrix elements in the single-electron representation and then transforming the matrices into the  $LS$  representation. The resulting matrices were then diagonalized. The value of the crystalline field parameter  $Dq$  and the positions of the energy levels are found to be in good agreement with the experimental results of McClure.

#### INTRODUCTION

PARAMAGNETIC resonance of trivalent iron in various crystal symmetries has been reported in the literature.<sup>1-5</sup>  $\text{Fe}^{3+}$  ion in  $\text{Al}_2\text{O}_3$  is known to be under the influence of a trigonal crystalline field. Thus, the spectrum of the ferric ion may be analyzed in terms of a Hamiltonian whose terms must reflect the symmetry of the crystalline electric field. Low<sup>6</sup> has conducted a systematic investigation of the paramagnetic resonance and optical absorption spectra of the transition group

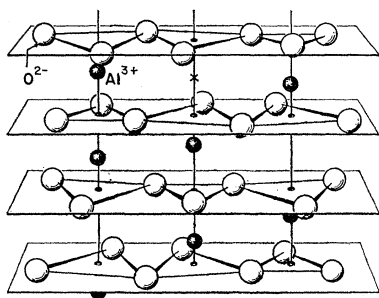


FIG. 1. A portion of the  $\text{Al}_2\text{O}_3$  lattice.

elements in cubic fields. Recently, McClure<sup>7</sup> published an extensive article on the optical spectra of transition metal ions in corundum. Present calculations, based on the point-charge model, give a value of the crystalline field parameter  $Dq$  (as defined by McClure<sup>7</sup> for trigonal fields) which agrees very well with the experimental value.<sup>7</sup>

The free ion  $\text{Fe}^{3+}$  has the configuration  $3d^5$   $^6S$ ;  $^4G$ ,  $^4P$ ,  $^4D$ , and  $^4F$  are the first-four excited states. The position of the excited levels were obtained from *Atomic-Energy Levels*.<sup>8</sup> For trigonal symmetry one needs three parameters to describe the crystalline field. A portion of the  $\text{Al}_2\text{O}_3$  lattice as described by Geschwind and Remeika<sup>9</sup> is shown in the Fig. 1. The over-all symmetry is only  $C_3$ . Group-theoretical considerations show that all the orbital degeneracy should be removed under this symmetry. However, we have treated the symmetry as  $C_{3v}$ , which is allowed when dealing with  $d$  electrons.

#### CALCULATIONS OF THE WAVE FUNCTIONS OF THE EXCITED STATES

The wave functions of the excited states are determined by the methods developed by Condon and Shortley.<sup>10</sup> The easiest wave function to write down unambiguously is that of  $^4G$  state having the maximum

<sup>1</sup> B. Bleaney and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 1 (1954).

<sup>2</sup> W. Low, Proc. Phys. Soc. (London) **B69**, 837 (1956).

<sup>3</sup> L. S. Kornienko and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **33**, 805 (1957) [translation: Soviet Phys.—JETP **6**, 620 (1958)].

<sup>4</sup> G. S. Bogle and H. F. Symmon, Proc. Phys. Soc. (London) **B73**, 631 (1959).

<sup>5</sup> D. Carter and A. Okaya, Phys. Rev. **118**, 1485 (1960).

<sup>6</sup> W. Low, Phys. Rev. **118**, 1136 (1960). (Other references are contained in this paper.)

<sup>7</sup> D. S. McClure, J. Chem. Phys. **36**, 2757 (1962).

<sup>8</sup> C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467.

<sup>9</sup> S. Geschwind and J. P. Remeika, Phys. Rev. **122**, 757 (1961).

<sup>10</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), p. 227.

TABLE I. Transformation matrix from uncoupled to coupled representation.

	$ a, 3/2, 3\rangle$	$ b, 3/2, 3\rangle$		$ a, 3/2, 2\rangle$	$ b, 3/2, 2\rangle$	$ c, 3/2, 2\rangle$
${}^4G, 3/2, 3\rangle$	$(1/2)^{1/2}$	$(1/2)^{1/2}$	${}^4G, 3/2, 2\rangle$	$(3/14)^{1/2}$	$-(3/14)^{1/2}$	$-(4/7)^{1/2}$
${}^4F, 3/2, 3\rangle$	$(1/2)^{1/2}$	$-(1/2)^{1/2}$	${}^4F, 3/2, 2\rangle$	$(1/2)^{1/2}$	$(1/2)^{1/2}$	0
			${}^4D, 3/2, 2\rangle$	$(2/7)^{1/2}$	$-(4/7)^{1/2}$	$(3/7)^{1/2}$
	$ a, 3/2, 3\rangle \equiv   +2^+ -2^+ +2^- +1^+0^+ \rangle$			$ a, 3/2, 2\rangle \equiv   +2^+ -2^+ +2^- +1^+ -1^+ \rangle$		
	$ b, 3/2, 3\rangle \equiv   +2^+ +1^+ -1^+ +1^+0^+ \rangle$			$ b, 3/2, 2\rangle \equiv   +2^+ +1^+ -1^+0^+0^- \rangle$		
	${}^4G, 3/2, 4\rangle \equiv   +2^+ +2^- +1^+ -1^+0^+ \rangle$			$ c, 3/2, 2\rangle \equiv   +2^+ -2^+ +1^+ +1^- +0 \rangle$		
			${}^6S, 5/2, 0\rangle \equiv   +2^+ -2^+ +1^+ -1^+0^+ \rangle$			
	$ a, 3/2, 0\rangle$	$ b, 3/2, 0\rangle$	$ c, 3/2, 0\rangle$	$ d, 3/2, 0\rangle$	$ e, 3/2, 0\rangle$	
${}^6S, 3/2, 0\rangle$	$-(1/5)^{1/2}$	$+(1/5)^{1/2}$	$-(1/5)^{1/2}$	$+(1/5)^{1/2}$	$+(1/5)^{1/2}$	
${}^4G, 3/2, 0\rangle$	$-(1/70)^{1/2}$	$+(1/70)^{1/2}$	$-(16/70)^{1/2}$	$-(16/70)^{1/2}$	$(36/70)^{1/2}$	
${}^4F, 3/2, 0\rangle$	$-(1/10)^{1/2}$	$-(1/10)^{1/2}$	$+(4/10)^{1/2}$	$+(4/10)^{1/2}$	0	
${}^4D, 3/2, 0\rangle$	$-(4/14)^{1/2}$	$(4/14)^{1/2}$	$(1/14)^{1/2}$	$-(1/14)^{1/2}$	$-(4/14)^{1/2}$	
${}^4P, 3/2, 0\rangle$	$-(4/10)^{1/2}$	$(4/10)^{1/2}$	$(1/10)^{1/2}$	$(1/10)^{1/2}$	0	
	$ a, 3/2, 0\rangle \equiv   -2^+ +2^- +1^+ -1^+0^+ \rangle$			$ c, 3/2, 0\rangle \equiv   +2^+ -2^+ -1^+ +1^+0^+ \rangle$		
	$ b, 3/2, 0\rangle \equiv   +2^+ -2^- +1^+ -1^+0^+ \rangle$			$ d, 3/2, 0\rangle \equiv   +2^+ -2^+ +1^+ -1^+0^- \rangle$		
				$ e, 3/2, 0\rangle \equiv   +2^+ -2^+ +1^+ -1^+0^- \rangle$		
	$ a, 3/2, 1\rangle$	$ b, 3/2, 1\rangle$	$ c, 3/2, 1\rangle$	$ d, 3/2, 1\rangle$		
${}^4G, 3/2, 1\rangle$	$(3/7)^{1/2}$	$(3/7)^{1/2}$	$-(1/14)^{1/2}$	$+(1/14)^{1/2}$		
${}^4F, 3/2, 1\rangle$	$(2/10)^{1/2}$	$-(2/10)^{1/2}$	$-(3/10)^{1/2}$	$-(3/10)^{1/2}$		
${}^4D, 3/2, 1\rangle$	$-(1/14)^{1/2}$	$-(1/14)^{1/2}$	$-(6/14)^{1/2}$	$+(6/14)^{1/2}$		
${}^4P, 3/2, 1\rangle$	$(3/10)^{1/2}$	$-(3/10)^{1/2}$	$+(2/10)^{1/2}$	$+(2/10)^{1/2}$		
	$ a, 3/2, 1\rangle \equiv   +2^+ -2^+ -1^+ +1^+ +1^- \rangle$			$ c, 3/2, 1\rangle \equiv   +2^+ -2^+ +2^- -1^+0^+ \rangle$		
	$ b, 3/2, 1\rangle \equiv   +2^+ -2^+ +1^+0^+0^- \rangle$			$ d, 3/2, 1\rangle \equiv   +2^+ +1^+ -1^+ -1^+0^+ \rangle$		

value of  $M_L$ :

$$|{}^4G, 4\rangle = | +2^+ +2^- +1^+ -1^+0^+ \rangle, \quad (1)$$

where the notation on the right-hand side of the above equation stands for an antisymmetric wave function in which the first electron has  $m_l = +2$  and spin up, the second electron has  $m_l = +2$  and spin down, and so on. By applying the lowering operator  $L_x - iL_y$  to Eq. (1), one obtains  $|{}^4G, 3\rangle$  as a linear combination of certain other antisymmetrical wave functions,

$$|{}^4G, 3\rangle = (1/\sqrt{2}) | +2^+ -2^+ +2^- +1^+0^+ \rangle + (1/\sqrt{2}) \times | +2^+ +1^+ -1^+ +1^+0^+ \rangle. \quad (2)$$

The state  $|{}^4F, 3\rangle$  can be expressed as a linear combination of the same component functions orthogonalized to  $|{}^4G, 3\rangle$ . In this way one can obtain all the wave functions of  $3d^5$  configuration and these are shown in Table I.

#### CRYSTALLINE POTENTIAL

The general form of the crystalline potential  $V$ , for a trigonal field showing a distortion along the  $[111]$  direction is given by the following expression<sup>11</sup>:

$$V = A_0^2 (R_1, \Theta_1, \Phi_1; R_2, \Theta_2, \Phi_2; \dots R_6, \Theta_6, \Phi_6) r_i^2 Y_2^0(\theta_i, \phi_i) + A_4^0 (R_1, \Theta_1, \Phi_1; \dots R_6, \Theta_6, \Phi_6) r_i^4 Y_4^0(\theta_i, \phi_i) + A_4^3 (R_1, \Theta_1, \Phi_1; \dots R_6, \Theta_6, \Phi_6) r_i^4 Y_4^3(\theta_i, \phi_i) + A_4^{-3} (R_1, \Theta_1, \Phi_1; \dots R_6, \Theta_6, \Phi_6) r_i^4 Y_4^{-3}(\theta_i, \phi_i). \quad (3)$$

<sup>11</sup> B. Bleaney and K. W. H. Stevens, Rept. Progr. Phys. (London) **16**, 108 (1953).

The  $R_j$ ,  $\Theta_j$ , and  $\Phi_j$  are the coordinates of the  $j$ th oxygen ion with respect to the ion nucleons. The  $\theta_i$ ,  $\phi_i$ , and  $r_i$  are the coordinates of the  $i$ th electron of iron ion referred to the same origin. The sum in Eq. (3) is over the five  $3d$  electron. The values for  $R$ ,  $\Theta$ , and  $\Phi$  for the two positions of the metal ion, (a)  $\text{Fe}^{3+}$  ion at the  $\text{Al}^{3+}$  site and (b)  $\text{Fe}^{3+}$  ion displaced by 0.1 Å towards the empty octahedral site, are shown in Table II. The values used for the position (a) were those established for  $\text{Al}_2\text{O}_3$ .<sup>9</sup>

The  $A_l m$ 's in the Eq. (3) are obtained by calculating the lattice sum of Eq. (4),

$$A_l m = \left[ \frac{4\pi}{2l+1} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} \sum_j \frac{e_j}{R_j^{l+1}} P_l^m(\cos\Theta_j) \cos m\Phi_j, \quad (4)$$

TABLE II. Coordinates of oxygen atoms, with respect to origin at the aluminum nucleus. [See text for the explanation of positions (a) and (b).]

	Oxygen ion	O-O Distance (in Å units)	Al-O Distance (in Å units)		$\Theta$		$\Phi$
			(a)	(b)	(a)	(b)	
Lower triangle	O <sub>1</sub>	2.881	1.845	1.804	115°48'	112°58'	60°
	O <sub>2</sub>						300°
	O <sub>3</sub>						180°
Upper triangle	O <sub>4</sub>	2.495	1.988	2.059	46°27'	44°25'	0°
	O <sub>5</sub>						120°
	O <sub>6</sub>						240°

TABLE III. The values of the crystalline field parameters.

	$A_2^0$ ( $10^{14}$ esu/cm <sup>3</sup> )	$A_4^0$ ( $10^{30}$ esu/cm <sup>5</sup> )	$A_4^{\pm 3}$ ( $10^{31}$ esu/cm <sup>5</sup> )
Position (a)	0.337187	0.743864	-0.117368
Position (b)	0.725323	0.536017	-0.113605

where the sum is over the six neighboring oxygen ions and  $e_j$  is the charge on each of the oxygen ion. The resulting values are shown in the Table III.

#### MATRIX ELEMENTS OF THE CRYSTALLINE FIELD

We need to calculate the matrix elements of the form

$$\langle L, M | V | L', M' \rangle. \quad (5)$$

This leads to a ( $24 \times 24$ ) matrix. But matrix elements in Eq. (5) vanish unless  $M' = M$  or  $M' = M \pm 3$ . Thus, the ( $24 \times 24$ ) matrix is reduced to three ( $8 \times 8$ ) matrices. In what follows, we shall refer to these matrices as I, II, and III.

Since the potential is of the form  $\sum_{i=1}^5 v_i$ , its matrix elements are expressible in terms of those of a single electron.

The states involved in matrices I, II, and III are shown in Table IV. Owing to the Hermitian character

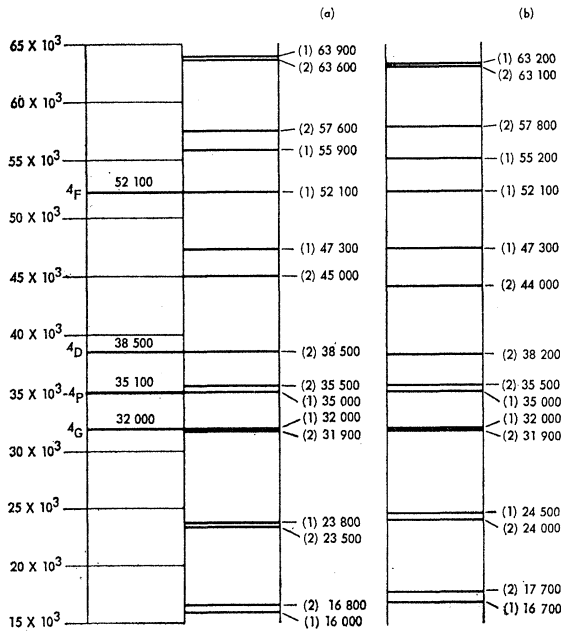


FIG. 2. Energy levels of  $\text{Fe}^{3+}$  in  $\text{Al}_2\text{O}_3$  for two positions of the  $\text{Fe}^{3+}$  ion (see text). Left-hand side shows the positions of the energy levels in free ion. Brackets in front of the values gives the degeneracy.

TABLE IV. States involved in the matrices I, II, and III. (See text.)

Matrix I	Matrix II	Matrix III
$ ^4G, 4\rangle$	$ ^4G, 3\rangle$	$ ^4G, 2\rangle$
$ ^4G, 1\rangle$	$ ^4G, 0\rangle$	$ ^4G, -1\rangle$
$ ^4G, -2\rangle$	$ ^4G, -3\rangle$	$ ^4G, -4\rangle$
$ ^4F, 1\rangle$	$ ^4F, 3\rangle$	$ ^4F, 2\rangle$
$ ^4F, -2\rangle$	$ ^4F, 0\rangle$	$ ^4F, -1\rangle$
$ ^4D, 1\rangle$	$ ^4F, -3\rangle$	$ ^4D, 2\rangle$
$ ^4D, -2\rangle$	$ ^4D, 0\rangle$	$ ^4D, -1\rangle$
$ ^4P, 1\rangle$	$ ^4P, 0\rangle$	$ ^4P, -1\rangle$

of these matrices, it is enough to calculate the matrix elements on one side of the diagonal.

The nonvanishing elements are shown in Table V. Single-electron matrix elements are evaluated by the

TABLE V. Transformation of the matrix elements in the coupled representation to the single-electron matrix elements.

Matrix I
$\langle 4, 4   V   3, 1 \rangle = (6/5)^{1/2} \langle 1   V   -2 \rangle$
$\langle 4, 4   V   1, 1 \rangle = -(4/5)^{1/2} \langle 1   V   -2 \rangle$
$\langle 4, 1   V   3, 1 \rangle = (3/35)^{1/2} [2 \langle 2   V   2 \rangle + \langle 1   V   1 \rangle - 2 \langle 0   V   0 \rangle]$
$\langle 4, 1   V   3, -2 \rangle = -(6/7)^{1/2} \langle 1   V   -2 \rangle$
$\langle 4, 1   V   1, 1 \rangle = -(2/35)^{1/2} [2 \langle 2   V   2 \rangle - 4 \langle 1   V   1 \rangle + 3 \langle 0   V   0 \rangle]$
$\langle 4, -2   V   3, 1 \rangle = (6/35)^{1/2} \langle -1   V   2 \rangle$
$\langle 4, -2   V   3, -2 \rangle = -(3/7)^{1/2} [2 \langle 2   V   2 \rangle - \langle 0   V   0 \rangle]$
$\langle 4, -2   V   1, 1 \rangle = (7/5)^{1/2} \langle -2   V   1 \rangle$
$\langle 3, 1   V   2, 1 \rangle = (2/35)^{1/2} [3 \langle 2   V   2 \rangle - 4 \langle 1   V   1 \rangle + \langle 0   V   0 \rangle]$
$\langle 3, 1   V   2, -2 \rangle = (10/7)^{1/2} \langle 1   V   -2 \rangle$
$\langle 3, -2   V   2, 1 \rangle = (1/7)^{1/2} \langle -2   V   1 \rangle$
$\langle 3, -2   V   2, -2 \rangle = -(4/7)^{1/2} [2 \langle 2   V   2 \rangle - \langle 0   V   0 \rangle]$
$\langle 2, 1   V   1, 1 \rangle = -(3/35)^{1/2} [2 \langle 2   V   2 \rangle - \langle 1   V   1 \rangle - \langle 0   V   0 \rangle]$

#### Matrix II

$$\begin{aligned} \langle 4, 3 | V | 3, 3 \rangle &= \langle 2 | V | 2 \rangle - \langle 1 | V | 1 \rangle \\ \langle 4, 3 | V | 3, 0 \rangle &= (1/5)^{1/2} \langle 1 | V | -2 \rangle \\ \langle 4, 3 | V | 1, 0 \rangle &= (9/5)^{1/2} \langle 1 | V | -2 \rangle \\ \langle 4, 0 | V | 3, 3 \rangle &= (5/7)^{1/2} \langle -1 | V | 2 \rangle \\ \langle 4, 0 | V | 3, -3 \rangle &= (5/7)^{1/2} \langle 2 | V | -1 \rangle \\ \langle 4, -3 | V | 3, 0 \rangle &= -(1/5)^{1/2} \langle -1 | V | 2 \rangle \\ \langle 4, -3 | V | 3, -3 \rangle &= -[\langle 2 | V | 2 \rangle - \langle 1 | V | 1 \rangle] \\ \langle 4, -3 | V | 1, 0 \rangle &= (9/5)^{1/2} \langle -2 | V | 1 \rangle \\ \langle 3, 3 | V | 2, 0 \rangle &= (9/7)^{1/2} \langle 2 | V | -1 \rangle \\ \langle 3, -3 | V | 2, 0 \rangle &= (9/7)^{1/2} \langle -1 | V | 2 \rangle \end{aligned}$$

#### Matrix III

$$\begin{aligned} \langle 4, 2 | V | 3, 2 \rangle &= (3/7)^{1/2} [2 \langle 2 | V | 2 \rangle - \langle 0 | V | 0 \rangle] \\ \langle 4, 2 | V | 3, -1 \rangle &= (6/35)^{1/2} \langle 2 | V | -1 \rangle \\ \langle 4, 2 | V | 1, -1 \rangle &= (7/5)^{1/2} \langle 2 | V | -1 \rangle \\ \langle 4, -1 | V | 3, 2 \rangle &= (6/7)^{1/2} \langle -1 | V | 2 \rangle \\ \langle 4, -1 | V | 3, -1 \rangle &= -(3/35)^{1/2} [2 \langle 2 | V | 2 \rangle + \langle 1 | V | 1 \rangle - 2 \langle 0 | V | 0 \rangle] \\ \langle 4, -1 | V | 1, -1 \rangle &= (2/35)^{1/2} [2 \langle 2 | V | 2 \rangle - 4 \langle 1 | V | 1 \rangle + 3 \langle 0 | V | 0 \rangle] \\ \langle 4, -4 | V | 3, -1 \rangle &= -(6/5)^{1/2} \langle -1 | V | 2 \rangle \\ \langle 4, -4 | V | 1, -1 \rangle &= (4/5)^{1/2} \langle -1 | V | 2 \rangle \\ \langle 3, 2 | V | 2, 2 \rangle &= (4/7)^{1/2} [2 \langle 2 | V | 2 \rangle - \langle 0 | V | 0 \rangle] \\ \langle 3, 2 | V | 2, -1 \rangle &= -(1/7)^{1/2} \langle 2 | V | -1 \rangle \\ \langle 3, -1 | V | 2, 2 \rangle &= -(10/7)^{1/2} \langle -1 | V | 2 \rangle \\ \langle 3, -1 | V | 2, -1 \rangle &= -(2/35)^{1/2} [3 \langle 2 | V | 2 \rangle - 4 \langle 1 | V | 1 \rangle + \langle 0 | V | 0 \rangle] \\ \langle 2, -1 | V | 1, -1 \rangle &= (3/35)^{1/2} [2 \langle 2 | V | 2 \rangle - \langle 1 | V | 1 \rangle - \langle 0 | V | 0 \rangle] \end{aligned}$$

TABLE VI. Hamiltonian matrix.

Matrix I								
	${}^4G, 4$	${}^4G, 1$	${}^4G, -2$	${}^4P, 1$	${}^4D, 1$	${}^4D, -2$	${}^4F, 1$	${}^4F, -2$
$\langle {}^4G, 4  $	32 000	0	0	7935	0	0	-9719	0
$\langle {}^4G, 1  $	0	32 000	0	7952	0	0	5145	8214
$\langle {}^4G, -2  $	0	0	32 000	-10 498	0	0	3673	-4849
$\langle {}^4P, 1  $	7935	7952	-10 498	35 100	-1360	0	0	0
$\langle {}^4D, 1  $	0	0	0	-1360	38 500	0	-4411	-3353
$\langle {}^4D, -2  $	0	0	0	0	0	38 500	-10 604	-5599
$\langle {}^4F, 1  $	-9719	5145	3673	0	-4411	-10 604	52 100	0
$\langle {}^4F, -2  $	0	8214	-4849	0	-3353	-5599	0	52 100
Matrix II								
	${}^4G, 3$	${}^4G, 0$	${}^4G, -3$	${}^4P, 0$	${}^4D, 0$	${}^4F, 3$	${}^4F, 0$	${}^4F, -3$
$\langle {}^4G, 3  $	32 000	0	0	-11 903	0	-2761	-3968	0
$\langle {}^4G, 0  $	0	32 000	0	0	0	7498	0	7498
$\langle {}^4G, -3  $	0	0	32 000	-11 903	0	0	-3968	2761
$\langle {}^4P, 0  $	-11 903	0	-11 903	35 100	0	0	0	0
$\langle {}^4D, 0  $	0	0	0	0	38 500	10 060	0	10 060
$\langle {}^4F, 3  $	-2761	7498	0	0	10 060	52 100	0	0
$\langle {}^4F, 0  $	-3968	0	-3968	0	0	0	52 100	0
$\langle {}^4F, -3  $	0	7498	2761	0	10 060	0	0	52 100
Matrix III								
	${}^4G, 2$	${}^4G, -1$	${}^4G, -4$	${}^4P, -1$	${}^4D, 2$	${}^4D, -1$	${}^4F, 2$	${}^4F, -1$
$\langle {}^4G, 2  $	32 000	0	0	-10 498	0	0	4849	3673
$\langle {}^4G, -1  $	0	32 000	0	-7952	0	0	8214	-5145
$\langle {}^4G, -4  $	0	0	32 000	7935	0	0	0	-9719
$\langle {}^4P, -1  $	-10 498	-7952	7935	35 100	0	1360	0	0
$\langle {}^4D, 2  $	0	0	0	0	38 500	0	5599	-10 604
$\langle {}^4D, -1  $	0	0	0	1360	0	38 500	-3353	4411
$\langle {}^4F, 2  $	4849	8214	0	0	5599	-3353	52 100	0
$\langle {}^4F, -1  $	3673	-5145	-9719	0	-10 604	4411	0	52 100

operator equivalence method of Stevens.<sup>12</sup>

$$\begin{aligned} \langle l, m' | v | l, m \rangle = & \frac{1}{2} (5/4\pi)^{1/2} A_2 \alpha r^2 (3m^2 - 6) \delta_{m', m} + \frac{1}{8} (9/4\pi)^{1/2} \\ & \times A_4 \beta r^4 (35m^4 - 155m^2 + 72) \delta_{m', m} \\ & + 315 (9/7! \pi)^{1/2} A_4 \beta r^4 (2m + 3) \delta_{m', m+3} \\ & + 315 (9/7! \pi)^{1/2} A_4^{-3} \beta r^4 (2m - 3) \delta_{m', m-3}, \end{aligned}$$

where  $\alpha$  and  $\beta$  are, respectively,  $-2/21$  and  $2/63$  for a single  $d$  electron;  $\langle r^2 \rangle$  and  $\langle r^4 \rangle$  designate the radial part of the matrix elements and were calculated assuming the wave function of a  $d$  electron to be hydrogen-like. This leads to

$$\langle r^k \rangle = \frac{1}{6!} \left( \frac{3a_0}{2Z_{\text{eff}}} \right)^k \Gamma(k+7), \quad (6)$$

where  $Z_{\text{eff}} = 6.25$  is the effective charge of the Fe nucleus,<sup>13</sup> and  $a_0$  is the Bohr radius. Thus,

$$\begin{aligned} \langle r^2 \rangle &= 9.03 \times 10^{-17} \text{ cm}^2, \\ \langle r^4 \rangle &= 1.31 \times 10^{-32} \text{ cm}^4. \end{aligned}$$

Substituting these values and  $A$ 's from Eq. (4) in Eq. (5), one obtains the values of nonvanishing single-

electron matrix elements which can be used to calculate matrix elements occurring in Table V. The Hamiltonian matrix is completed by placing the following values of the free trivalent iron ion:

$$\begin{aligned} {}^4G &= 32\,000 \text{ cm}^{-1}, \\ {}^4P &= 35\,100 \text{ cm}^{-1}, \\ {}^4D &= 38\,500 \text{ cm}^{-1}, \\ {}^4F &= 52\,100 \text{ cm}^{-1}, \end{aligned}$$

in the matrices obtained above. These values arise from the free-ion part of the total Hamiltonian. The resulting matrices for position (a) are shown in Table VI.

## RESULTS

The six matrices, three for each position of the metal ion, were diagonalized by means of an IBM-7090 computer to obtain the energy levels of trivalent iron in aluminum oxide crystal. These are shown in the Fig. 2. The degeneracy of the various levels is compatible with the results expected from group-theoretical considerations. The value of  $Dq$  in the two cases was found to be 1880 and 1820  $\text{cm}^{-1}$ , respectively, which

<sup>12</sup> K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

<sup>13</sup> J. C. Slater, Phys. Rev. **36**, 57 (1930).

TABLE VII. Comparison between theoretical and experimental values for various transitions. All transitions originate from the state  ${}^6A_{1g}$ . The values are given in  $\text{cm}^{-1}$ .

Transition	Theoretical	Experimental	Experimental values for $\text{Fe}^{3+}$ in beryl
${}^6A_{1g} \rightarrow {}^4T_1t^4e$	16 700	not observed	14 200
$\rightarrow {}^4T_2t^4e$	17 700	17 200	17 500
		17 800	
$\rightarrow {}^4Eg^2$	24 000	25 600	23 600
${}^4A_1t^3e^2$			
$\rightarrow {}^4T_1t^3e^2$	24 500	not observed	26 500

compares well with the experimental value of  $1650 \text{ cm}^{-1}$  obtained by McClure.<sup>7</sup>

Table VII shows the comparison between our calculated values [for position (b)] of the energy levels and those obtained experimentally by McClure.<sup>7</sup> The last column in Table VI gives the values for  $\text{Fe}^{3+}$  in beryl.<sup>14</sup> We quote these values because in beryl also  $\text{Fe}^{3+}$  is coordinated with six oxygen ions and the average Al—O distance is  $1.94 \text{ \AA}$  which is fairly close to the Al—O distance in corundum.

<sup>14</sup> M. Duir and W. Low, Phys. Rev. **119**, 1587 (1960).

## DISCUSSION

Though our calculations are in good agreement with the experimental results, it is obvious that the present model will not lead to the correct spectra of other transition metal ions in  $\text{Al}_2\text{O}_3$  because of the strong  $Z_{\text{eff}}$  dependence of  $\langle r^k \rangle$  [See Eq. (6)]. The alternative method of calculating is to use Watson's<sup>15</sup> functions. The values so obtained vary less strongly from one transition metal ion to the other, but are unrealistically low, for example, for  $\text{Fe}^{3+}$  Watson's functions give  $\langle r^2 \rangle = 0.32 \times 10^{-16} \text{ cm}^2$ ,  $\langle r^4 \rangle = 0.22 \times 10^{-32} \text{ cm}^4$ , and  $Dq = 300 \text{ cm}^{-1}$ . A recent note by Artman and Murphy<sup>16</sup> on ruby takes into account the shift of the neighboring  $\text{O}^{2-}$  ions due to the shift of the  $\text{Cr}^{3+}$  ion along the  $C$  axis. One should really expect different amounts of displacements for different ions substituted in  $\text{Al}_2\text{O}_3$ . This effect, along with the fact that the changes in the configuration of the surrounding ions are caused due to the substitutional ion being in an excited state, might lead to a model which gives good results for all the transition metal ions.

<sup>15</sup> R. E. Watson, Technical Report No. 12, 1959, Solid State and Molecular Theory Group MIT, Cambridge, Massachusetts.

<sup>16</sup> J. O. Artman and J. C. Murphy, Bull. Am. Phys. Soc. **8**, 313 (1963).

## Thermal Conductivity of III-V Compounds at High Temperatures\*

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The thermal conductivity of intrinsic and heavily doped InAs crystals was determined between 300 and  $900^\circ\text{K}$  using the diffusivity technique. The electronic contribution was computed using the measured electrical conductivity and the Seebeck coefficient. Adding  $3 \times 10^{19}$  donors and acceptors  $\text{cm}^{-3}$  to the intrinsic InAs increases the lattice thermal resistivity appreciably. Thermal conductivity data are given also for GaAs and InP. The anharmonicity parameters  $\chi$  of the III-V compounds, obtained by comparing the experimental thermal conductivities with the theoretical values of Leibfried and Schlömann for 3-phonon processes, are found to be temperature- and mass-ratio-dependent. The temperature dependence is believed to be caused by higher order processes. The correlation between the anharmonicity parameters and the mass ratios of the constituent elements of the compounds is ascribed to an effect of optical-mode scattering on the lattice thermal resistivity.

### A. INTRODUCTION

THE III-V compounds represent particularly suitable materials for studying the high-temperature thermal conductivity since they cover a wide range of values of the parameters influencing this property.

The present work is a detailed experimental investigation of the thermal conductivity of InAs. Previous measurements of this substance have been made by

Bowers *et al.*<sup>1</sup> and Stuckes.<sup>2</sup> This study was undertaken to extend the measurements on intrinsic material to higher temperatures as well as to investigate the effect of donor and acceptor impurities on the lattice thermal conductivity of InAs. This latter effect was observed earlier<sup>3</sup> in Ge.

<sup>1</sup>R. Bowers, R. W. Ure, J. E. Bauerle, and A. J. Cornish, J. Appl. Phys. **30**, 930 (1959).

<sup>2</sup>A. D. Stuckes, Phil. Mag. **5**, 84 (1960).

<sup>3</sup>D. S. Beers, G. D. Cody, and B. Abeles, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and The Physical Society, London, 1962), p. 41.

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