# Chemical Potential and Low-Lying Excitations in the Many-Boson System. II

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The approximate description of a many-boson system by its density fluctuations is considered. The representation of the chemical potential by a scattering matrix is compared with an exact solution in one dimension. It is found to be valid exactly in the low coupling limit and valid to within 10% for intermediate coupling strengths. In the case treated, the ground-state properties are given quite accurately for intermediate coupling strengths. The excitation spectrum is described less accurately. The velocity of sound obtained from the slope of the phonon spectrum is formally different from that obtained using the compressibility. Here, the sound velocities obtained from the two methods are found to agree numerically. Data for actual He<sup>4</sup> and a simple linear approximation to the density dependence of the scattering matrix are used. The sound velocity obtained is in rough agreement with the experimentally observed velocity in liquid He<sup>4</sup>.

# I. INTRODUCTION

 $\mathbf{N}$  a previous paper<sup>1</sup> we have described a formulation of the energy spectrum of the many-boson system in terms of density fluctuations. We assumed an unspecified macroscopic occupation of the zero-momentum state. There was no assumption about the density of the system.

Applications of the formalism gave two principal results. First, we obtained a representation of the chemical potential of the boson system by a scattering matrix. Second, we assumed Feynman's variational states to be the exact eigenstates and obtained a phonon spectrum for the elementary excitations. This held even for a system with negative zero-momentum scattering amplitude, as is the case for actual liquid He<sup>4</sup>.

In this paper we check that the results predicted by our formalism are correct in order of magnitude. The procedure we use is the following. We assume two things: First, the interparticle potential can be expanded in terms of a t matrix [the simplest form for tis the one we assumed in Eq. (19) of SB]. Second, we assume the Feynman state is nearly the true excited state. Combining these two, we obtained, in SB, a self-consistent set of equations for the excited-state energy [Eq. (30) of SB)] and the *t* matrix [Eq. (19)]. Here we solve the set of self-consistent equations in a special one-dimensional case. We compare our prediction for the chemical potential in this case with an exact solution which has been given by Lieb and Liniger.<sup>2,3</sup> Then, as a second comparison, we calculate the sound velocity for actual liquid He<sup>4</sup>. Experimental data for the chemical potential of liquid He<sup>4</sup> and the second virial coefficient of gaseous He<sup>4</sup> are used, thus avoiding the self-consistent calculation of the t matrix. The velocity is derived both from the slope of the calculated phonon spectrum and from the compressibility. These values are compared with each other and with the experimental value for the velocity.

## II. COMPARISON WITH AN EXACT SOLUTION FOR A ONE-DIMENSIONAL SYSTEM

Lieb and Liniger<sup>2</sup> have given an exact solution for a special case of interacting bosons. The case they treat is a one-dimensional system of bosons interacting through a two-body delta-function potential

 $v(x) = 2c\delta(x)$ .

We shall compare the values of the chemical potential, the ground-state energy, the excitation spectrum, and the sound velocity in the medium which are obtained with the scattering matrix of SB with their exact results in this case. The discussion is divided into two parts. Part A treats the properties of the system which are associated with the ground state. Part B treats the properties which are related to the excitation spectrum. The reason for the division is that the SB formalism treats the ground-state properties much more accurately than the excitation spectrum in this case. This presumably is due to the fact that the excitation spectrum obtained by Lieb<sup>3</sup> in this case has two separate types of excitation while we only assume the phonon spectrum.

To facilitate comparison we use, in this section only, the same notation as Lieb and Liniger<sup>2</sup>:

$$2m = 1,$$
  

$$\sum_{q} = \frac{L}{2\pi} \int_{-\infty}^{\infty} dq,$$
  

$$\rho = N/L,$$
  

$$\hbar = 1,$$

coupling parameter  $\gamma = c/\rho$ . N is the total number of bosons; L is the length in which they are contained. m is the mass of one boson.

#### **A.** Ground-State Properties

The expression for the chemical potential given in SB was [Eq. (20)]

$$\mu = N t_0, \qquad (1)$$

<sup>&</sup>lt;sup>1</sup> K. Sawada and L. W. Bruch, Phys. Rev. 131, 1379 (1963); this paper is referred to as SB here. <sup>2</sup> E. H. Lieb and W. Liniger, Phys. Rev. **130**, 1605 (1963). <sup>3</sup> E. H. Lieb, Phys. Rev. **130**, 1616 (1963).

where the scattering matrix is given by  $[Eq. (19) \Lambda$  is obtained using its defining equation, in SB7

$$t_{q} = v_{q} + \sum_{q'} v_{q-q'} (1/-W_{q'}) t_{q'},$$
  
$$v_{q} = \frac{1}{L} \int e^{iqx} 2c\delta(x) dx = \frac{2c}{L}.$$
 (2)

Assuming that the Feynman state is the true excited state, we have from Eqs. (21) and (30) of SB

$$\frac{1}{-W_q} = \frac{q^2}{-\bar{\omega}_q(\bar{\omega}_q+q^2)},$$

where

$$\tilde{\omega}_q = [q^4 + 2q^2\Lambda_q]^{1/2}$$

and

$$\Lambda_{q}^{2} = \int_{0}^{N} 2N' t_{q}^{2}(N') dN'.$$
(3)

For the delta-function potential, v has constant momentum-space components. We obtain a t with constant momentum-space components. (Hence,  $\Lambda_q$  is independent of q; we write it as  $\Lambda$ .)

$$t = 2c/L - \sum_{q} \frac{2c}{L} \frac{q^2}{(q^4 + 2q^2\Lambda)^{1/2}} \frac{t}{\left[(q^4 + 2q^2\Lambda)^{1/2} + q^2\right]}$$
$$= \frac{2c}{L} / \left\{ 1 + \frac{c}{\pi} \int_{-\infty}^{\infty} dq \frac{q^2}{(q^4 + 2q^2\Lambda)^{1/2}} \frac{1}{\left[(q^4 + 2q^2\Lambda)^{1/2} + q^2\right]} \right\},$$
$$t = \frac{2c}{L} / \left[ 1 + \frac{c}{\pi} \left(\frac{2}{\Lambda}\right)^{1/2} \right].$$
(4)



FIG. 1. The roots of Eq. (17) as a function of the coupling strength. The limiting behavior is  $x \cong \pi^2/2\gamma$  as  $\gamma \to 0$  and  $x \cong \pi^4/4\gamma^2$ as  $\gamma \to \infty$ . These are the two straight lines in this figure.

$$2\Lambda \frac{d}{dN} \Lambda = 2Nt^2(N) = 2N \left(\frac{2c}{L}\right)^2 / \left[1 + \frac{c}{\pi} \left(\frac{2}{\Lambda}\right)^{1/2}\right]^2.$$

Then integration over N gives

$$\Lambda^2 + (8\sqrt{2}/3\pi)\gamma\rho\Lambda^{3/2} + (4\gamma^2\rho^2/\pi^2)\Lambda = 4\rho^4\gamma^2.$$
 (5)

We introduce a dimensionless parameter x,

$$x = (\pi^2/4\gamma^2\rho^2)\Lambda.$$
 (6)

Equation (5) becomes an equation in x,

$$x^{2} + \frac{1}{3} 4\sqrt{2} x^{3/2} + x = \pi^{4}/4\gamma^{2}.$$
 (7)

The solution in the strong-coupling limit,  $\gamma \rightarrow \infty$ , is

$$x=\pi^4/4\gamma^2, \quad \Lambda=\pi^2\rho^2.$$
 (8)



FIG. 2. Comparison of the SB value of the chemical potential with the values of Lieb and Liniger for intermediate couplings. The solid line is taken from the paper of Lieb and Liniger. The marked points are calculated SB values.

The solution in the weak-coupling limit,  $\gamma \rightarrow 0$ , is

$$x = \pi^2/2\gamma$$
,  $\Lambda = 2\gamma\rho^2$ . (9)

The general solution to Eq. (7) obtained numerically is given in Fig. 1.

The chemical potential in these limits is

$$\mu = Nt = 2\rho^2 \gamma / [1 + (2x)^{-1/2}] = 2\rho^2 \gamma \quad \text{as} \quad \gamma \to 0$$
$$= \sqrt{2}\pi^2 \rho^2 \quad \text{as} \quad \gamma \to \infty .$$
(10)

The weak-coupling answer is exactly that of Lieb and Liniger.<sup>2</sup> The strong-coupling answer of Lieb and Liniger<sup>2</sup> is

$$\mu = \pi^2 \rho^2$$
 as  $\gamma \to \infty$ .

Our value is  $\sqrt{2}$  times this answer.

Lieb and Liniger have solved numerically for the value of the chemical potential for coupling parameters in the range 0-3. We have solved Eq. (7) numerically for x corresponding to this range. Our values of the

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chemical potential in this region agree with the values given by Lieb and Liniger to within 5%. We plot our results in Fig. 2.

The ground-state energy is also given quite accurately. Lieb and Liniger<sup>2</sup> express the ground-state energy in terms of another function,  $e(\gamma)$ , defined by

$$e = E/N\rho^2$$
.

The exact  $e(\gamma)$  has the property that  $e \to \frac{1}{3}\pi^2$  as  $\gamma \to \infty$ . Using our formula (10) for the chemical potential, the SB formalism gives

$$\mu(N) = \rho^2 f(\gamma)$$
, where  $f(\gamma) = 2\gamma / [1 + (2x)^{-1/2}]$ .

Since

$$E(\gamma) = \int_{0}^{N} \mu(N') dN' = N \rho^{2} \int_{1}^{\infty} \frac{f(\gamma z)}{z^{4}} dz, \qquad (11)$$



FIG. 3. Comparison of ground-state energy results,  $E_0 = N\rho^2 e(\gamma)$ .  $e(\gamma)$  is plotted against coupling strength. Curve 1 is the result of the SB calculation and has asymptotic value  $e \to \sqrt{2}\frac{1}{3}\pi^2$  as  $\gamma \to \infty$ . Curve 2 is the result of the exact Lieb and Liniger calculation and has asymptotic value  $e \to \frac{1}{3}\pi^2$  as  $\gamma \to \infty$ . Curves 3 and 4 (given by Lieb and Liniger) are the result of zero-order perturbation theory and Bogoliubov perturbation theory, respectively.

then

$$e(\gamma) = \int_1^\infty \frac{f(\gamma z)}{z^4} dz.$$

In the strong-coupling limit,  $\gamma \rightarrow \infty$ , according to (10),

$$\mu = \rho^2 \sqrt{2} \pi^2$$

and

Therefore,

$$f(\gamma z) = \sqrt{2}\pi^2.$$
$$e_{\gamma \to \infty} = \int_{1}^{\infty} \sqrt{2} \frac{\pi^2}{z^4} dz = \frac{1}{3}\pi^2 \sqrt{2}$$

This is a factor  $\sqrt{2}$  larger than the exact value. For intermediate couplings we have evaluated the integral for  $e(\gamma)$  numerically. A comparison of the SB results with the exact results and with the results of a Bogo-liubov calculation (given by Lieb and Liniger) is given



FIG. 4. Comparison of the sound-velocity results. The reduced sound velocity,  $c/\rho$ , is plotted against coupling strength. Curve 1 is the exact result of Lieb. This exact result coincides, up to  $\gamma \approx 10$ , with sound velocity calculated from the compressibility using either SB theory or the Bogoliubov expression for the ground-state energy. Curve 3 is the sound velocity derived from the slope of the SB excitation spectrum. Curve 2 is the sound velocity derived from the slope of the Bogoliubov excitation spectrum (given by Lieb).

in Fig. 3. The accuracy (compared to the exact calculation) is better than 10% up to  $\gamma \approx 10$ .

Another quantity which tests the accuracy of the ground state is the sound velocity, *c*, in the medium. In this section, we obtain this from the compressibility,

$$c^2 = 2\rho \frac{d}{d\rho} \mu.$$

We evaluate this numerically, using Eqs. (7) and Eq. (10). The velocity derived from the compressibility (from our  $\mu$ ) does not differ detectably from Lieb's<sup>3</sup> solution for couplings up to  $\gamma \approx 7.5$ . Lieb's solution is given in Fig. 4.

#### B. Properties of the Excitation Spectrum

We compare our excitation spectrum with that of Lieb<sup>3</sup> (Bogoliubov branch). If we introduce the reduced momentum used by Lieb,

$$y=q/\rho$$
,

$$\omega = \rho^2 \left( y^4 + \frac{2\Lambda}{\rho^2} y^2 \right)^{1/2}.$$
 (12)

In the weak-coupling limit,  $\gamma \rightarrow 0$ ,

then

$$\omega = \rho^2 (y^4 + 4\gamma y^2)^{1/2}$$

This agrees with the exact result. In the strong-coupling limit  $\gamma \rightarrow \infty$ ,

$$\omega = \rho^2 (y^4 + 2\pi^2 y^2)^{1/2}$$

This gives a slope of the phonon spectrum for small y which is a factor  $\sqrt{2}$  smaller than the exact result.

We have plotted a comparison of the energies of our solution and the exact solution in Fig. 5. In the figure



FIG. 5. Comparison of SB excitation energy with the exact value given by Lieb. The comparison is made for two fixed values of the reduced momentum  $y=q/\rho$ . The reduced excitation energy  $\omega/\rho^2$  is plotted against the coupling constant. (a) y=1; the asymptotic values for  $\gamma \to \infty$  are  $(\omega/\rho^2)_{\rm LL}=7.5$  and  $(\omega/\rho^2)_{\rm BB}=4.6$ . (b) y=4; the asymptotic values for  $\gamma \to \infty$  are  $(\omega/\rho^2)_{\rm LL}=41$  and  $(\omega/\rho^2)_{\rm SB} = 24.$ 

we have plotted excitation energy against the coupling constant for a few values of the momentum. Using agreement between the exact and approximate energies as a criterion, we see deviations due to our error in the strong-coupling limit already become notable for  $\gamma \approx 3$  for the excitation energy. At least part of our error comes from the assumed form for t. When treated exactly, t will depend on the momentum and the energy denominator  $1/(-W_q')$  in (3) will have a qdependence.

The sound velocity in the medium may also be obtained from the slope of the phonon spectrum:

$$c = \rho (2\Lambda/\rho^2)^{1/2}$$

This has been evaluated numerically and a comparison of the results with the exact solution by Lieb<sup>3</sup> is given in Fig. 4. The velocity derived from the calculated phonon spectrum is lower than the exact result, but it is still accurate to about 10% for coupling strengths up to  $\gamma \approx 7.5$ .

Therefore, to summarize, the formalism of SB gives the correct energies in the weak-coupling limit and energies which are of the correct order of magnitude in the strong-coupling limit. In a range of intermediate coupling ( $\gamma$  varying from 1 to 5 here) the formalism of SB gives energies accurate to better than 10%. In the case treated here, the ground-state properties are given quite well by the SB formalism. The properties of the excitation spectrum are less well treated, but this may be due to the existence (in this case) of a class of excitations which were averaged out in the SB formalism.

Finally, we remark that the assumption of macroscopic occupation,  $n_0$ , of the zero-momentum state made in SB is satisfied here. Girardeau<sup>4</sup> has obtained a macroscopic occupation for the case of a one-dimensional Bose system with very strong interparticle repulsions. He finds

$$n_0 \propto N/\ln N$$
,  
 $N_q \propto \frac{N^2}{L^2 \ln N} \frac{1}{q} \rightarrow 0$  for finite  $q$ 

The SB formalism gives this result in a wide range of coupling constants. More detailed considerations on  $n_0$  will be given elsewhere.<sup>5</sup>

# III. SOUND VELOCITY IN LIQUID He<sup>4</sup>

We may calculate the sound velocity either from the compressibility or from the slope of the phonon spectrum. Both require a knowledge of the density dependence of the zero-momentum scattering matrix,  $t_0$ . We do not obtain this dependence here. Instead, we approximate it by a linear dependence.

We fit a straight line to the values of  $t_0$  at the actual liquid He<sup>4</sup> density and  $t_0$  for two-body scattering. The first value of  $t_0$  is obtained from the chemical potential. The two-body scattering value is based on experimental data for the second virial coefficient of He<sup>4</sup> gas.

The quantity we work with is  $\Omega t_0$  ( $\Omega$ =volume). All numbers are in cgs units.

We use the expression for the chemical potential  $\mu$ given in SB:

$$\mu = Nt_0$$
.

Using<sup>6</sup>  $\mu = -9.25 \times 10^{-16}$  erg at the density of liquid He<sup>4</sup>,  $n=2.2\times10^{22}/\text{cm}^3$ , we have  $\Omega t_0=-4.2\times10^{-38}$ .

For the two-body  $t_0$ , the method to be described here leaves uncertainties. However, we believe it gives the correct order of magnitude.

<sup>&</sup>lt;sup>4</sup> M. Girardeau, J. Math. Phys. 1, 516 (1960).

 <sup>&</sup>lt;sup>6</sup> L. Bruch (to be published).
 <sup>6</sup> K. R. Atkins, *Liquid Helium* (Cambridge University Press, New York, 1959).

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FIG. 6. De Boer's results for s-wave phase shift as a function of momentum. The dashed straight line through his lowest k value gives the minimum slope used in determining  $t_0$ .  $\delta_0$  is plotted against  $k\sigma$  ( $\sigma$ =2.56 Å).

De Boer<sup>7</sup> has fitted the temperature dependence of the second virial coefficient of  $He^4$  gas by assuming a Lennard-Jones potential as the interaction between  $He^4$  atoms:

where

$$V(r) = 4\epsilon [(1/R^{12}) - (1/R^6)],$$

$$R = r/\sigma$$
;  $\epsilon = 14.04 \times 10^{-16} \text{ erg}$ ;  $\sigma = 2.56 \text{ Å}$ .

He has calculated the phase shifts for two He<sup>4</sup> atoms scattering via this potential. We give his results for the s-wave phase shift,  $\delta_0$ , in Fig. 6.

We take the two-body  $t_0$  as determined mostly by the s-wave contribution and have

$$t_0 = \lim_{k \to 0} \left( \frac{-4\pi\hbar^2}{m\Omega} \right) \frac{\tan \delta_0}{k}$$

De Boer's curve for  $\delta_0$  has not yet turned to the origin at his lowest calculated point. We assume there is no two-body bound state in the potential. Then  $\delta_0=0$  at k=0 and we get a lower bound to  $\lim_{k\to 0} (\tan \delta_0)/k$  by taking the slope of the dashed line in Fig. 6. (If we fit a cubic polynomial through de Boer's 3 lowest values of  $\delta_0$  this value for the slope changes by about a factor of 2.)

Then we have

$$\Omega t_0 = -2.31 \times 10^{-37}, n=0.$$

The straight line fitted to these two values of  $\Omega t_0$  is<sup>8</sup>

 $\Omega t_0 = (n - n_0)\beta; \quad n_0 = 2.67 \times 10^{22} / \text{cm}^3; \quad \beta = 8.65 \times 10^{-60}.$ 

The sound velocity obtained from the compressibility

$$c^2 = \frac{1}{m} \frac{d}{dn} \mu = \frac{n}{m} \left( n \frac{d}{dn} \Omega t_0 + \Omega t_0 \right) = 5 \times 10^8;$$

 $c = 2.2 \times 10^4$  cm/sec at liquid He<sup>4</sup> density.

The sound velocity obtained from the slope of the phonon spectrum is

$$c^{2} = \frac{1}{m} \left\{ \int_{0}^{n} 2n' (\Omega t_{0}(n'))^{2} dn' \right\}^{1/2}$$
  
$$c = 1.95 \times 10^{4} \text{ cm/sec}.$$

These values agree with each other and with the experimental value  $c=2.4\times10^4$  cm/sec in order of magnitude. This is of special interest because the two theoretical expressions are formally different. In low orders in  $t_0$  the two expressions coincide for  $t_0>0$ . Our calculations here have been for the case  $t_0<0$ .

We may check the consistency of the approximations in fitting with a linear density dependence by calculating  $\mu$  and the equilibrium density.

The chemical potential was a piece of input data. If the system is at zero pressure we may recover it from

$$\mu = E_0 / N,$$

where the ground-state energy  $E_0$  is

$$E_0 \!=\! \int_0^N \mu dN' \!=\! \Omega \! \int_0^n n'(\Omega t_0) dn'$$
 This gives

$$E_0/N = -1.17 \times 10^{-15}$$
 erg.

The experimental value (for zero pressure) used was  $\mu = 0.92 \times 10^{-15}$  erg, in reasonable agreement with the above value.

The equilibrium density is obtained from a calculation of the pressure exerted by the system

$$p = n^2 (d/dn) (E_0/N) = \frac{1}{2} n^2 (\frac{4}{3}n - n_0)\beta;$$

p=0 for  $n=\frac{3}{4}n_0\approx 2.00\times 10^{22}/\text{cm}^3$ ; this is roughly the observed density of  $2.2\times 10^{22}/\text{cm}^3$ .

These two checks convince us that the order-ofmagnitude agreement obtained for the sound velocities is more than fortuitous. We believe that this agreement confirms the validity of the theoretical approximations made in deriving the phonon spectrum. Once again, these assumptions were the large occupation, with small fluctuations, of the zero-momentum state; the validity of the expansion of v in terms of our simple t matrix; and

<sup>&</sup>lt;sup>7</sup> J. de Boer and A. Michels, Physica 6, 409 (1939).

<sup>&</sup>lt;sup>8</sup> We do not know the exact dependence which this linear fit approximates since we have not solved the self-consistent *t*-matrix equations for actual He<sup>4</sup>. We hope to carry out the self-consistent solution in the near future. In this section we show that the assumed form for  $\Omega t_0$  gives values for  $\mu$ ,  $c^2$ , and the equilibrium density of He<sup>4</sup> which are consistent with experiment. The assumed dependence for  $\Omega t_0$  is similar to that which was found in a selfconsistent calculation for a Bose gas interacting through a hardcore potential [K. A. Brueckner and K. Sawada, Phys. Rev. 106, 1128 (1957)]. Figure 1 of this reference shows an approximate

quadratic dependence of  $\lambda^2(\propto \rho\Omega t_0)$  on  $\rho a^3$  for small  $\rho a^3$ . The *t* matrix used by Brueckner and Sawada has the same energy denominator in the low- and high-momentum limits as the *t* matrix used in SB. Addition of an attractive interaction<sup>¬</sup> to the hard-sphere repulsion of Brueckner and Sawada can be anticipated to extend the quadratic dependence to a much larger range of  $\rho$ .

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 He<sup>4</sup>. 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.

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# **Optical Spectra of Trivalent Iron in Trigonal Fields**

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The energy levels of Fe<sup>3+</sup> in Al<sub>2</sub>O<sub>3</sub> 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 LSrepresentation. 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> Fe<sup>3+</sup> ion in Al<sub>2</sub>O<sub>3</sub> 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



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

- Teor. Fiz. 33, 805 (1957) [translation: Soviet Thys.—JEIT 0, 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.)

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.7

The free ion Fe<sup>3+</sup> has the configuration  $3d^5$  <sup>6</sup>S; <sup>4</sup>G,  ${}^{4}P$ ,  ${}^{4}D$ , and  ${}^{4}F$  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 Al<sub>2</sub>O<sub>3</sub> 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  $C_{3\nu}$ , 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  ${}^{4}G$  state having the maximum

<sup>&</sup>lt;sup>2</sup> W. Low, Proc. Phys. Soc. (London) **B69**, 837 (1956). <sup>3</sup> L. S. Kornienko and A. M. Prokhorav, Zh. Eksperim. i Teor. Fiz. 33, 805 (1957) [translation: Soviet Phys.—JETP 6,

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

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

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

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