

## Three-Body-Force Shell Model and the Lattice Dynamics of Magnesium Oxide

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The expression for the three-body potential in ionic solids, derived quantum mechanically by Lundqvist, has been obtained classically by assuming a deformation in the charge-density distribution due to overlap of the nearest-neighbor electron cloud. A reexamination of the effect of this potential on the lattice dynamics of ionic solids has revealed an error in the original formulation of the so-called three-body-force shell model which has now been eliminated. The application of the corrected equations to MgO, with only the oxygen ion assumed polarizable, results in dispersion curves which present a good agreement with the neutron spectroscopic data.

### I. INTRODUCTION

Verma and Singh<sup>1</sup> have recently developed a three-body-force shell model (TSM) based on Lundqvist's expression<sup>2</sup> for the lattice potential. The model uses a function  $f(a)$  of the nearest-neighbor separation  $a$  connected with the overlap integrals of electron wave functions and its space derivative  $df/da$  as parameters, in addition to the usual parameters of the simple shell model.<sup>3</sup> On classical considerations one can show that the TSM takes account of the charge transfer between neighboring ions in addition to the dipoles induced on the ion sites, while the simple shell model accounts only for the induced dipoles (Cochran<sup>4</sup>). An error in the formulation of the TSM has been recently pointed out by Agarwal and Verma<sup>5</sup> which concerns the definition of shell and core charges. By redefining the shell and core charges suitably, it is still possible to obtain the basic equations of the model as they have been described before but the meanings of the electrical and distortion polarizabilities become somewhat different. It is therefore necessary to reformulate the model correctly and to investigate the extent to which this correction affects the results obtained earlier in various lattice dynamical studies.<sup>6-11</sup>

Cochran<sup>4</sup> has recently shown that the TSM is equivalent to another variation of the shell model, viz., the breathing shell model (BSM).<sup>12,13</sup> A simple classical derivation of Lundqvist's expression<sup>2</sup> for the lattice potential of ionic solids and a proof of the equivalence of the TSM and BSM have been recently obtained by Verma<sup>14</sup> by reinterpreting an analysis of the breathing motion of the shells in the BSM presented by Basu and Sengupta.<sup>15</sup> This interpretation leads to a charge transfer implied in Lundqvist's lattice potential and is in agreement with Cochran's analysis of the TSM.

The classical derivation of the lattice potential as given by Verma<sup>14</sup> and the necessary correction in the TSM are briefly described in Sec. II and the

results obtained by applying the corrected TSM equations on MgO are given in Sec. III. The choice of this solid is dictated by the circumstance that it has been recently investigated by Singh and Upadhyaya<sup>16</sup> on the basis of the original TSM equations and is expected to show prominent differences in the numerical results obtained by the two sets of equations in view of the large Cauchy discrepancy with which the three-body forces are directly related. The valence of the ions also leads to a major difference between the two sets of equations; this difference being much larger for the divalent MgO than for the monovalent alkali halides.

### II. THEORY

Let us designate the ions in an ionic lattice structure with two atoms per unit cell by the usual symbol  $(l, \kappa)$ , where the cell index  $l$  is the integer triplet  $(l_1, l_2, l_3)$  and the basis index  $\kappa = 1, 2$ . The charge-density distribution  $\rho_{l\kappa}$  around an ion can be expressed as a function of position relative to the corresponding nucleus,

$$\rho_{l\kappa} = \rho_{l\kappa}(\vec{r}) .$$

In view of the translational symmetry,  $\rho_{l\kappa}(\vec{r})$  will be independent of  $l$  in the ideal undisturbed state of the lattice and may be considered as a function of the scalar distance from the corresponding nucleus:

$$\rho_{l\kappa}^0(\vec{r}) = \rho_{l\kappa}^0(r) . \quad (1)$$

In the state of vibration, the ions move out of their equilibrium configurations causing a change in the charge-density function which can now be expressed as a series in spherical harmonics. Thus,

$$\begin{aligned} \delta\rho_{l\kappa}(\vec{r}) &= \rho_{l\kappa}(\vec{r}) - \rho_{l\kappa}^0(r) \\ &= f_0(r) + \sum_m f_{1m}(r)Y_{1m} + \sum_m f_{2m}(r)Y_{2m} + \dots \quad (2) \end{aligned}$$

The first term represents an isotropic scalar deformation of the charge cloud, the second a di-

pole deformation, and so on. The simple shell model<sup>3</sup> accounts for only the second term in the expansion. If we retain only the first two terms in Eq. (2) and assume that the charge on an ion remains unaltered during the vibrations, we obtain

$$\int_0^{\infty} 4\pi r^2 f_0(r) dr = 0. \quad (3)$$

Equation (3) is identically satisfied by a simple function

$$f_0(r) = (1 + a_{1\kappa})^3 g(r + a_{1\kappa}r) - g(r), \quad (4)$$

where  $g(r)$  is an arbitrary function and  $a_{1\kappa}$  is a parameter. By choosing  $g(r) = \rho_{\kappa}^0(r)$ , one obtains

$$4\pi r^2 dr \rho_{1\kappa}(r) = 4\pi r^2 dr' \rho_{\kappa}^0(r'), \quad (5)$$

where

$$r' = r + a_{1\kappa}r.$$

Equation (5) represents the breathing motion implied in the breathing shell model.

This interpretation of the breathing motion of the shells depends entirely on the result (3), which is valid only if the upper limit of integration on the charge-density distribution is extended to infinity. In a solid the ions (or atoms) are fairly close together and the total space can be divided among various ions by suitably drawn dividing surfaces. In an ionic solid where the charge-density distribution is to a large extent spherically symmetric around each nucleus, the positive- and negative-ion spaces can be conveniently divided in spheres of ionic radii  $r_{\kappa}$  centered at the corresponding lattice points. The charge belonging to  $\kappa$ -type ion will therefore be determined by

$$\int_0^{r_{\kappa}} [\rho_{\kappa}^0(r) + f_0(r)] 4\pi r^2 dr, \quad (6)$$

where the upper limit is now  $r_{\kappa}$  instead of  $\infty$ . Even in a static lattice the proximity of the ions will cause a deformation of the charge clouds owing to the overlap of electron wave functions. It is this deformation that has been considered by Lundqvist and is thus implied in the TSM. Let us define the original charge on the ion in absence of the deformation  $f_0(r)$  to be  $Z_{\kappa}$ :

$$\int_0^{r_{\kappa}} \rho_{\kappa}^0(r) 4\pi r^2 dr = Z_{\kappa}. \quad (7)$$

Substituting in (6) the expression (4) with  $g(r) = \rho_{\kappa}^0$  and assuming  $a_{1\kappa}$  to be small, we obtain for the charge on a  $\kappa$ -type ion

$$\int_0^{r_{\kappa}} (1 + a_{1\kappa})^3 \rho_{\kappa}^0(r + a_{1\kappa}r) 4\pi r^2 dr \simeq Z_{\kappa} + \bar{a}_{1\kappa} Z_{\kappa},$$

where

$$\bar{a}_{1\kappa} = 4\pi r_{\kappa}^3 \rho_{\kappa}^0(r_{\kappa}) a_{1\kappa} / Z_{\kappa}.$$

The charge neutrality over the unit cell demands

$$\sum_{\kappa} (Z_{\kappa} + \bar{a}_{1\kappa} Z_{\kappa}) = 0. \quad (8)$$

Since  $\bar{a}_{1\kappa}$  is a parameter which will vary with the proximity of neighboring ions, Eq. (8) implies

$$Z_1 = -Z_2 \quad \text{and} \quad \bar{a}_{11} = \bar{a}_{12}.$$

It appears as though a charge  $\bar{a}_{1\kappa} Z_1$  is transferred from the negative ion to the positive ion of the same cell. In effect, each ion will have a charge transferred to it from all its neighbors so that  $\bar{a}_{1\kappa}$  can be supposed to be the sum total of such transfers. If we neglect overlap between ions farther than the first,  $\bar{a}_{1\kappa}$  will not have any contribution from second and higher neighbors. In a static lattice we can therefore consider this parameter to be independent not only of  $\kappa$  but also of  $l$ . Denoting the charge on the positive ion by  $Z (= |Z_{\kappa}|)$ , we can write the charge on the ions as  $\pm Z[1 + \bar{a}(r)]$ .

The Coulomb energy per unit cell of this modified charge system will be

$$- \alpha_m e^2 Z^2 [1 + \bar{a}(r)]^2 / r$$

and if we neglect the square of  $\bar{a}(r)$  we can write the energy per unit cell of the ionic solid as

$$\varphi = - \alpha_m e^2 Z [Z + 12f(r)] / r + 12V(r), \quad (9)$$

where  $V(r)$  is the overlap repulsive potential and we have put  $Z\bar{a}(r) = 6f(r)$  to obtain the expression given by Lundqvist for  $\varphi$ . The Coulomb pair potential coupling two ions at  $(l, \kappa)$  and  $(l', \kappa')$  will be

$$\begin{aligned} c\varphi_{(\kappa \kappa')}^{(l l')} &= \frac{Z_{\kappa} Z_{\kappa'} [1 + 6f(r)]^2}{r_{(\kappa \kappa')}^{(l l')}} \\ &\simeq \frac{Z_{\kappa} Z_{\kappa'}}{r_{(\kappa \kappa')}^{(l l')}} + \frac{12f(r) Z_{\kappa} Z_{\kappa'}}{r_{(\kappa \kappa')}^{(l l')}}. \end{aligned}$$

The first term is a central two-body potential identical with the conventional Coulomb potential of the rigid-ion model. The second term is also of the same type but its magnitude depends on  $f(r)$  which in its turn depends on the proximity of neighboring ions. Thus this potential contains the coordinates of atoms at  $(l, \kappa)$ ,  $(l', \kappa')$ , and all the nearest-neighboring sites of  $(l, \kappa)$ . In view of the dependence of this potential on the coordinates of three different ions of the solid, it is termed a three-body potential. Clearly, the three-body potential derived quantum mechanically by Lundqvist<sup>2</sup> implies a charge transfer between neighboring ions.

The consideration of the short-range overlap interaction and the long-range Coulomb interaction between shells and cores in the shell model leads to equations in which these interactions appear in distinct terms. The consideration of three-body interactions within the framework of the shell model can therefore be done in a simple way by including the three-body potential in the Coulomb-interaction terms. Inclusion of this potential leads to two additional terms in the coupling coefficients which depend on the second derivative of the poten-

tial. One of these terms that contains the second derivative of  $f(r)$  can be easily assimilated in the nearest-neighbor overlap potential whose parameters are to be determined phenomenologically. The other term represents a long-range three-body coupling which contains the first derivative of the function  $f(r)$  and has been evaluated by Verma and Singh.<sup>1</sup> The TSM equations are consequently obtained by modifying the Coulomb matrix  $\underline{C}$  of Woods *et al.*<sup>3</sup> to

$$\underline{C}' = Z[Z + 12f(a)]\underline{C} + \underline{V}, \quad (10)$$

where  $\underline{V}$  is the matrix corresponding to the terms containing the first derivative of the charge transfer function  $f(r)$ .

The Coulomb matrix appears in the equations of motion of the shell model in terms representing interactions between the cores, the shells, and the cores and the shells. These terms will contain the charges of the cores and shells as multiplying factors. The error in Verma and Singh's<sup>1</sup> model is that the Coulomb matrix has been modified everywhere according to Eq. (10), implying modification of all charges by the factor  $Z[Z + 12f(a)]$ , while the expression for polarizability defining the shell charge has not been suitably modified. Thus Verma and Singh<sup>1</sup> erroneously retain in their model, the expression for  $\alpha$  as

$$\alpha = e^2 Y^2 / (k + S_0). \quad (11)$$

The correct equations can be obtained in a simple way by suitably defining the core and the shell charges which have an arbitrary nature.

Since the charges including the transferred charge on the ions are  $Z_\kappa = \pm [Z + 6f(a)]$ , the core and shell charges should for convenience be assumed in the form  $X_\kappa [Z + 6f(a)]$  and  $Y_\kappa [Z + 6f(a)]$  such that  $X_\kappa + Y_\kappa = \pm 1$ . The Coulomb interaction between the cores and shells will now be easily obtained correctly by replacing the Coulomb matrix  $\underline{C}$  by  $\underline{C}'$  as suggested by Verma and Singh.<sup>1</sup> Thus the equations of the three-body-force shell model are restored, provided we assume the core and shell charges in the form suggested above. The polarizability equation will now be

$$\alpha_\kappa = e^2 Y_\kappa^2 Z [Z + 12f(a)] / (k_\kappa + S_0) \quad (12)$$

and the distortion polarizability can be defined by

$$d_\kappa = e Y_\kappa \{Z [Z + 12f(a)]\}^{1/2} / (k_\kappa + S_0). \quad (13)$$

The definitions of the core and shell charge given above enable us to express the total polarizability per unit cell in a simple way. Thus, we can write

$$\frac{\alpha + \alpha_I}{v} = \frac{P}{E} = \frac{1}{v} \left( \frac{Y^2}{k + S_0} + \frac{(1-d)^2}{R_0} \right) e^2 Z [Z + 12f(a)], \quad (14)$$

where the symbols used have the same meanings as in Woods *et al.*<sup>3</sup> Clearly, Eq. (14) can be ob-

tained from Eq. (2.3.11) of Woods *et al.* by replacing the charge  $e$  on the ion by  $eZ[Z + 6f(a)]$  and then by neglecting the square of  $f(a)$  as we have done before in deriving the expression for the potential energy. It may also be pointed out here that the original definition of the shell charges does not satisfy the consistency condition of the equations of motion and the present modified form eliminates this drawback (Sinha<sup>17</sup>).

The corrections required in the TSM are only in respect of Eqs. (12) and (13). These equations, however, modify the parameters of the theory substantially and in view of the successes of the TSM it is pertinent to investigate the consequences of this modification. To do this we have applied the corrected equations to the study of phonon dispersion in MgO which has recently been investigated by Singh and Upadhyaya.<sup>16</sup>

### III. CALCULATIONS AND RESULT

The basic equations for the calculation of the parameters are

$$C_{11} = \frac{e^2}{4a_0^4} \left[ -5.112Z[Z + 12f(a)] + A + 9.3204Z \left( a \frac{df}{da} \right) \right], \quad (15)$$

$$C_{12} = \frac{e^2}{4a_0^4} \left[ 0.226Z[Z + 12f(a)] - B + 9.3204Z \left( a \frac{df}{da} \right) \right], \quad (16)$$

$$C_{44} = \frac{e^2}{4a_0^4} \{2.556Z[Z + 12f(a)] + B\}, \quad (17)$$

$$B = -1.165Z[Z + 12f(a)], \quad (18)$$

$$\mu\omega_{TO}^2 = R_0' - \frac{4\pi}{3} \frac{e^2}{v} Z'^2 \frac{Z[Z + 12f(a)]}{f_T}, \quad (19)$$

$$\mu\omega_{LO}^2 = R_0' + \frac{8\pi}{3} \frac{e^2}{v} \frac{Z'^2}{f_L} Z \left[ [Z + 12f(a)] + 6 \left( a \frac{df}{da} \right) \right], \quad (20)$$

where

$$f_L = 1 + \frac{8\pi}{3} \frac{\alpha}{v} \frac{1}{Z[Z + 12f(a)]} Z \left[ [Z + 12f(a)] + 6 \left( a \frac{df}{da} \right) \right], \quad (21)$$

$$f_T = 1 - \frac{4}{3} \pi \alpha / v, \quad (22)$$

$$Z' = 1 - d_2 + d_1, \quad (23)$$

$$R_0' = R_0 - e^2 \left( \frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right), \quad (24)$$

$$R_0 = (e^2/v) (A + 2B). \quad (25)$$

These equations, together with Eq. (12) or (13) determine the parameters  $A$ ,  $B$ ,  $f(a)$ ,  $(adf/da)$ ,  $d_\kappa$ , and  $Y_\kappa$  of the theory. However, the calculation of the parameters leads to imaginary or negative values for the parameter  $d_1$  unless the positive-ion polarizability is chosen to be of the order of 0.005 or lower. Even the experimental values of the

TABLE I. Input data.

Constants	Values	Refs.
$C_{11}$ ( $10^{11}$ dyn cm $^{-2}$ )	28.92 (30.53)	Sangster <i>et al.</i> <sup>a</sup>
$C_{12}$ ( $10^{11}$ dyn cm $^{-2}$ )	8.79	Sangster <i>et al.</i> <sup>a</sup>
$C_{41}$ ( $10^{11}$ dyn cm $^{-2}$ )	15.46	Sangster <i>et al.</i> <sup>a</sup>
$\alpha$ ( $10^{-24}$ cm $^3$ )	1.742	Tessman <i>et al.</i> <sup>b</sup>
Lattice constant ( $10^{-8}$ cm)	4.213	U. S. Natl. Bur. Std. Circular No. 539
$\omega_L$ ( $10^{13}$ rad sec $^{-1}$ ) <sup>c</sup>	13.60	
$\omega_T$ ( $10^{13}$ rad sec $^{-1}$ )	7.462	Infrared absorption frequency
$\epsilon_0$	9.8	Szigeti <sup>d</sup>
$\epsilon_\infty$	2.95	Szigeti <sup>d</sup>

<sup>a</sup>Reference 18.<sup>b</sup>Reference 19.<sup>c</sup>Value calculated from the LST relation.<sup>d</sup>Reference 20.

polarizability of the Mg $^{++}$  ion is very low. We have therefore neglected this polarizability and have assumed only the negative ion to be polarizable. The number of parameters are now only six and can be calculated from Eqs. (16)–(20) and (12) or (13) dropping the expression for  $C_{11}$ .  $\omega_L$  and  $\omega_T$  can be taken from the neutron scattering results directly. However, since the measurements by Sangster *et al.*<sup>18</sup> for the longitudinal optic branch near  $q=0$  seem to have large errors, we have preferred to use values of  $\omega_L$  and  $\omega_T$  as derived from the optical data. The input data are given in Table I and the values of the parameters in Table II. These values of the parameters were used to calculate  $C_{11}$ . The calculated value has been shown in

TABLE II. Model parameters.

A	B	$f(a)$	$(adf/da)$	Y	d
32.0918	-4.4199	-0.0086	-0.1221	-1.6490	0.3463

brackets and agrees closely with the experimental value. The elements of the dynamical matrix were computed in the usual way for a number of wave vectors along the principle symmetry directions [100], [110], and [111]. The calculated frequencies have been plotted against  $q$  in Fig. 1, together with the inelastic neutron spectroscopic measurements of Sangster *et al.*<sup>18</sup>

The order of agreement obtained in the present study is the same as that obtained by Singh and Upadhyaya<sup>14</sup> and by Sangster *et al.*<sup>18</sup> The latter authors have used a breathing shell model. In view of the correction suggested in Sec. II it would seem somewhat strange that the original TSM equations have led to such excellent results on so many ionic crystals. Effectively, the original TSM parameters correspond to values of polarizabilities which are larger by a factor  $Z[Z+12f(a)]$ . For monovalent solids for which  $Z=1$ , this factor is of the order of 1 and can lead to only minor differences from the correct theory. For divalent solids, however, the factor is of the order of 4 and can in most cases make the calculations of the parameters impossible unless compensated for in some way. The main difficulty arises with the expression for  $f_L$  and  $f_T$  [Eqs. (21) and (22)] which strongly influence the calculations of  $R'_0$  and  $Z'$ . Singh and Upadhyaya<sup>14</sup> have in effect divided the  $\alpha C_1/v$  term in these expressions by  $Z^2$ , whereas

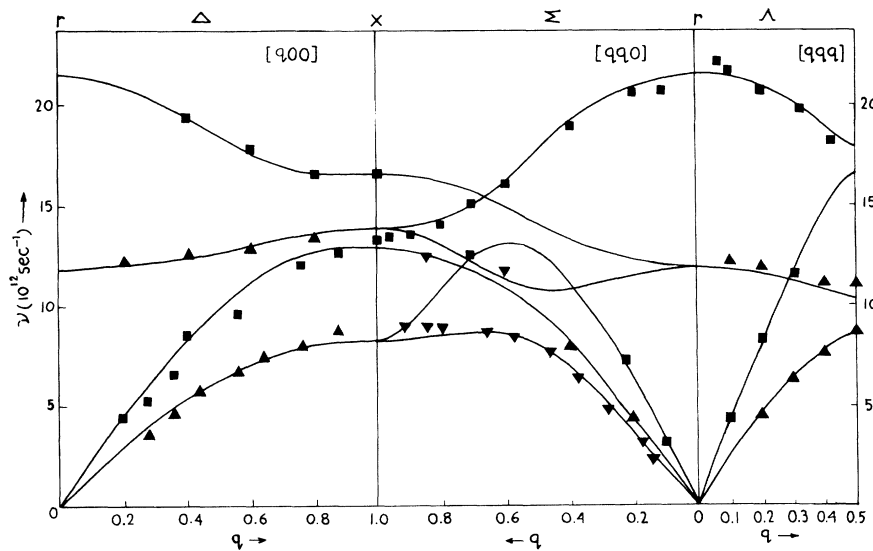


FIG. 1. Dispersion curves for MgO. The solid lines are theoretical curves;  $\blacksquare$ ,  $\blacktriangle$ , and  $\blacktriangledown$ , are experimental points from Sangster *et al.* (Ref. 18).

the correct calculation would require a division by  $Z[Z + 12f(a)]$ . Since  $f(a)$  is usually small, the two factors do not differ much and the phenomenological nature of the calculations can compensate for the small difference. This seems to be the explanation for the good agreements obtained by both the original and the corrected TSM equations.

The six-parameter TSM theory results in agreements at least as good as those of Sangster's *et al.*<sup>18</sup> eight-parameter model D. The ionic charge obtained in this model for the best fit with experimental curves is 1.918, which is not very different from 2. The  $Z_\kappa$  defined in the TSM is the charge contained in the sphere of radius  $r_\kappa$  ignoring isotropic deformation. This radius has a certain degree of arbitrariness and hence the charge  $Z$  of the TSM should be considered to be somewhat arbitrary. This means that this quantity should also be treated as a parameter and if enough equations are not available for its evaluation it may be determined by allowing it a free variation over a small range and by selecting the value for the best fit with the

experimental dispersion curves. The best value of  $Z_\kappa$  should logically be that derived from electron density maps integrated to a radius  $r_\kappa$  where the density acquires a minimum. This was the procedure used by Verma and Singh<sup>9</sup> in their study of lithium salts. Since our aim in the present work was mainly to correct the TSM equations for the defect mentioned above and the study of lattice dynamics of MgO was taken up for a check, we have contented ourselves by selecting a simple scheme for the study with  $Z = 2$ .

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