A Deformation Dipole Model for Crystals: Application to NaCl

D. D. Richardson[A,B] *and J. Mahanty*[A]

[A] Department of Theoretical Physics, Research School of Physical Sciences,
Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601.
[B] Present address: Materials Research Laboratories,
P.O. Box 50, Ascot Vale, Vic. 3032.

Abstract

We present a deformation dipole model based on theoretical calculations of induced moments in ion pairs. The model is generally applicable and in this paper is applied to the calculation of the lattice dynamics of NaCl. Only a few parameters are required to give good agreement with experiment. Limitations of the approach are discussed.

1. Introduction

In this paper we present a study of interatomic interactions in solids based on the deformation dipole model. In particular, we give as an example of its application a potential for sodium chloride and the consequent lattice dynamics, although the approach has wide applicability to other insulators. Both the deformation dipole model (Hardy and Karo 1979) and the shell model (Dick and Overhauser 1958) have been used in such problems for many years. In the shell model each ion in the crystal is treated as having a massive charged core, and a massless charged shell linked to the core by a spring. A non-Coulomb interaction is taken between the shells on adjacent ions and the remaining interaction is Coulombic between the various charges. The shell–core spring constant is fixed from the value of the ionic polarizability. In the deformation dipole model, the ionic polarizability is not linked to deformations directly—the deformation dipole moment on each ion is treated explicitly. Unlike the shell model, the deformation dipole model does not modify the non-Coulomb interaction at all. Both models reduce to the rigid-ion model of Kellermann (1940) in the limit of no polarizability or deformation.

Our model differs from that of Hardy and Karo (1979) in several respects. Firstly we have not made any changes to the non-Coulomb interaction to improve the rigid-ion model before introducing deformations. Hardy and Karo found it necessary to introduce angle-dependent forces. Our calculation uses strictly pairwise interactions. Finally, our choice of the parameters and functional forms for the deformation dipole moments on the ions in the crystal is based on recent theoretical work on induced moments in ion pairs (Lacey and Byers Brown 1974; Mahanty and Majumdar 1982). As a result of these refinements, we apparently need fewer parameters to fit our model to phonon dispersion curves than were needed by Hardy and Karo.

2. Formulation of the Model

If we assume that non-Coulombic force constants are described by a tensor $\mathbf{R}$ which is defined by

$$\mathbf{R} = \nabla\nabla\phi^{N}(r), \qquad (1)$$

where $\phi^{N}(r)$ is a non-Coulomb pair potential (e.g. a Born–Mayer form), then we may write the equation of motion for our crystal as

$$-m\ddot{u} = \mathbf{R} \cdot u - \mathbf{Z}' \cdot E. \qquad (2)$$

In equation (2) u are the ion displacements, m are their masses, $\mathbf{Z}'$ are the effective ion charges of the system (including deformation effects) and E is the electric field at each ion site.

Since the total dipole moment of the crystal is zero in equilibrium, we may expand the dipole moment for small ion displacements as

$$p = \sum_{i} p_{i} + \sum_{ij} (\nabla_{i}p_{j})u_{j} = \sum_{ij} (\nabla_{i}p_{j})u_{j}. \qquad (3)$$

We now write the instantaneous dipole moment of an ion in the form

$$p = (\mathbf{Z}+\varepsilon) \cdot u, \qquad (4)$$

where $Z_{\alpha\beta} = Z\delta_{\alpha\beta}$ for free ion charge Z, and ε represents the change in effective ion charge due to the deformation of the ion associated with its displacement. In general ε is not diagonal, and is similar to $\tilde{S}$ in equation (5.17) of Hardy and Karo (1979).

There is also a dipole moment, due to electronic polarization effects, of the form $\alpha \cdot E$, where α is the polarizability tensor. Thus equation (4) becomes

$$p = (\mathbf{Z}+\varepsilon) \cdot u + \alpha \cdot E. \qquad (5)$$

Using the relation (Cochran 1971)

$$E = -\mathbf{C} \cdot p, \qquad (6)$$

where $\mathbf{C}$ is such that the rigid-ion Coulomb dynamical matrix is (Kellermann 1940)

$$\mathbf{Z} \cdot \mathbf{C} \cdot \mathbf{Z}, \qquad (7)$$

we substitute into equation (5) to eliminate p, giving

$$E = -\mathbf{C}(\mathbf{Z}+\varepsilon) \cdot u - \mathbf{C}\alpha \cdot E, \qquad E = -(\mathbf{I}+\mathbf{C}\alpha)^{-1}\mathbf{C}(\mathbf{Z}+\varepsilon) \cdot u, \qquad (8a, b)$$

where $\mathbf{I}$ is the identity matrix.

Since the effective charge is $\mathbf{Z}' = \mathbf{Z}+\varepsilon$, our equation of motion (2) becomes

$$-m\ddot{u} = \mathbf{R} \cdot u + (\mathbf{Z}+\varepsilon)(\mathbf{I}+\mathbf{C}\alpha)^{-1}\mathbf{C}(\mathbf{Z}+\varepsilon) \cdot u. \qquad (9)$$

Thus in our deformation dipole model, the dynamical matrix is

$$\mathbf{D} = \mathbf{R}+(\mathbf{Z}+\varepsilon)(\mathbf{I}+\mathbf{C}\alpha)^{-1}\mathbf{C}(\mathbf{Z}+\varepsilon), \qquad (10)$$

with the phonon frequencies ω being given by the solutions of the determinantal equation

$$|\mathbf{m}\omega^2 - \mathbf{D}(\boldsymbol{q})| = 0, \tag{11}$$

where $\mathbf{D}(\boldsymbol{q})$ is the Fourier transform of equation (10) and $m_{ij} \equiv m_i \delta_{ij}$.

Cochran (1971) showed that the equivalent dynamical matrix for the shell model has the form

$$\mathbf{D} = \mathbf{R}^{\mathrm{sm}} + (\mathbf{Z} + \boldsymbol{\varepsilon}^{\mathrm{S}})(\mathbf{I} + \mathbf{C}\boldsymbol{\alpha}^{\mathrm{sm}})^{-1}\mathbf{C}(\mathbf{Z} + \boldsymbol{\varepsilon}^{\mathrm{S}}), \tag{12}$$

where $\mathbf{R}^{\mathrm{sm}}$ differs from $\mathbf{R}$ by a 'deformation term' and $\boldsymbol{\varepsilon}^{\mathrm{S}}$ are Szigeti charges. The polarizabilities $\boldsymbol{\alpha}^{\mathrm{sm}}$ are given in the shell model in terms of shell charges, spring constants and shell–shell terms.

The analogy between equations (10) and (12) is clear. Our deformation charges correspond to the Szigeti charges. In our model, also, $\mathbf{R}$ and $\boldsymbol{\alpha}$ are 'independent' of the deformation effects while they are all related in the shell model.

Equation (11) is also identical to equation (5.20) of Hardy and Karo (1979), except for the appearance of an extra $\mathbf{U}$ matrix in their equation—this is probably an error. Note that when we take $\boldsymbol{\varepsilon}$ to be zero, equation (11) reduces to the point polarizable model, and when $\boldsymbol{\alpha}$ are all zero we get Kellermann's rigid-ion model.

We have obtained expressions for the deformation charge $\boldsymbol{\varepsilon}$ as follows: There are basically two types of deformations likely on each ion—that between like ions and that between unlike ions. Both arise from exchange effects in a region of small overlap in the ionic crystal. The analysis of Mahanty and Majumdar (1982) (referred to as MM hereafter) of simple like and unlike atom pairs (H–H and H–He) can be extended to pairs of many-electron atoms or ions. Qualitatively it would be reasonable to expect from their work that for the case of a pair of unlike ions, with one considerably larger than the other, the dipole moment of the ith ion due to its interaction with the jth ion separated by the distance r_{ij} will be of the form

$$\boldsymbol{p}_i^{\mathrm{def}}(r_{ij}) = (\boldsymbol{r}_{ij}/r_{ij})G_{ij}\exp(-\lambda_{ij}r_{ij}), \tag{13}$$

where G_{ij} depends on the pair of ions and the range λ_{ij}^{-1} can be taken as the equivalent Born–Mayer range in $\mathbf{R}$. This exponential dependence may also be expected from the work of Lacey and Byers Brown (1974), when adapted to this problem.

For like ions a reasonable form would be

$$\boldsymbol{p}_i^{\mathrm{def}}(r_{ij}) = \boldsymbol{r}_{ij}\,e\,S^2(r_{ij})/2\{1 - S^2(r_{ij})\}, \tag{14}$$

where $S(r_{ij})$ is an overlap integral which varies from 1 to 0 monotonically as r_{ij} goes from zero to infinity. Its dependence on r_{ij} would be similar to that for a pair of hydrogen atoms:

$$S(r) = \{1 + (r/a_0) + \tfrac{1}{3}(r/a_0)^2\}\exp(-r/a_0).$$

Thus, we find the deformation charge from equation (3) as

$$\boldsymbol{\varepsilon} = \nabla \boldsymbol{p}^{\mathrm{def}}. \tag{15}$$

In our model then, we assume that λ in equation (13) is the same as that arising from a Born–Mayer type potential as used in R of equation (1). We have also assumed that we are free to vary the positive and negative ion polarizabilities α_+ and α_-, as well as the constants G_+ and G_- in equation (13). To account for the non-hydrogenic nature of like-ion deformations, we have also introduced a simple scaling factor a_0 into equation (14). Thus we have at most five free parameters.

Table 1. Calculated and experimental elastic constants for NaCl

$10 \text{ dyne cm}^{-2} = 1 \text{ Pa}$

| | Elastic constant (10^{12} dyne cm^{-2}) | |
	Calculated using CDN potential	Experimental results of Lewis *et al.*
C_{11}	0·584	0·573
C_{12}	0·137	0·112
C_{44}	0·136	0·133

3. Results

In doing our calculations we began by assuming that the rigid-ion calculation must be as accurate as possible to begin with. We tried to use the potential of Fumi and Tosi (1964) for NaCl, but found that it gave very poor results for both elastic constants (which are independent of ε and α) and the phonon dispersion curves. Much better results were obtained by using the potential given in Table 2 of Catlow *et al.* (1977; CDN hereafter), however, and this potential was subsequently used for all calculations. For this potential we derived the elastic constants given in Table 1, which show reasonable agreement with the experimental values of Lewis *et al.* (1967).

The phonon results for the CDN potential are similar to those given in Fig. 30*a* (curve RI) of Hardy and Karo (1979), although our CDN results give slightly better values, particularly for the TO modes. We took as our standard for comparison with experiment the results of Schmunk and Winder (1970), which appear to be generally consistent with the earlier work of Raunio *et al.* (1969).

The results of MM on H–H and H–He indicate that G increases with the ionic radius. Therefore, we have related G_+, G_- of equation (13) to the ionic radii phenomenologically as

$$G_+/G_- = r_+/r_- . \tag{16}$$

This reduces the number of parameters by one; G_- was chosen as the free parameter.

Also, in view of the universal relation for polarizabilities being proportional to the cube of ionic radius, we considered

$$\alpha_+/\alpha_- = (r_+/r_-)^3 , \tag{17}$$

thereby further reducing the number of parameters to two— namely G_- and α_-.

In practice, it proved difficult to make a fit to experiment on the basis of varying G_- and α_- subject to equations (16) and (17), and these latter two relations were relaxed. We also found it necessary to reduce equation (14) to a very low value to get good fits. Therefore, like-ion deformations can probably be ignored. We
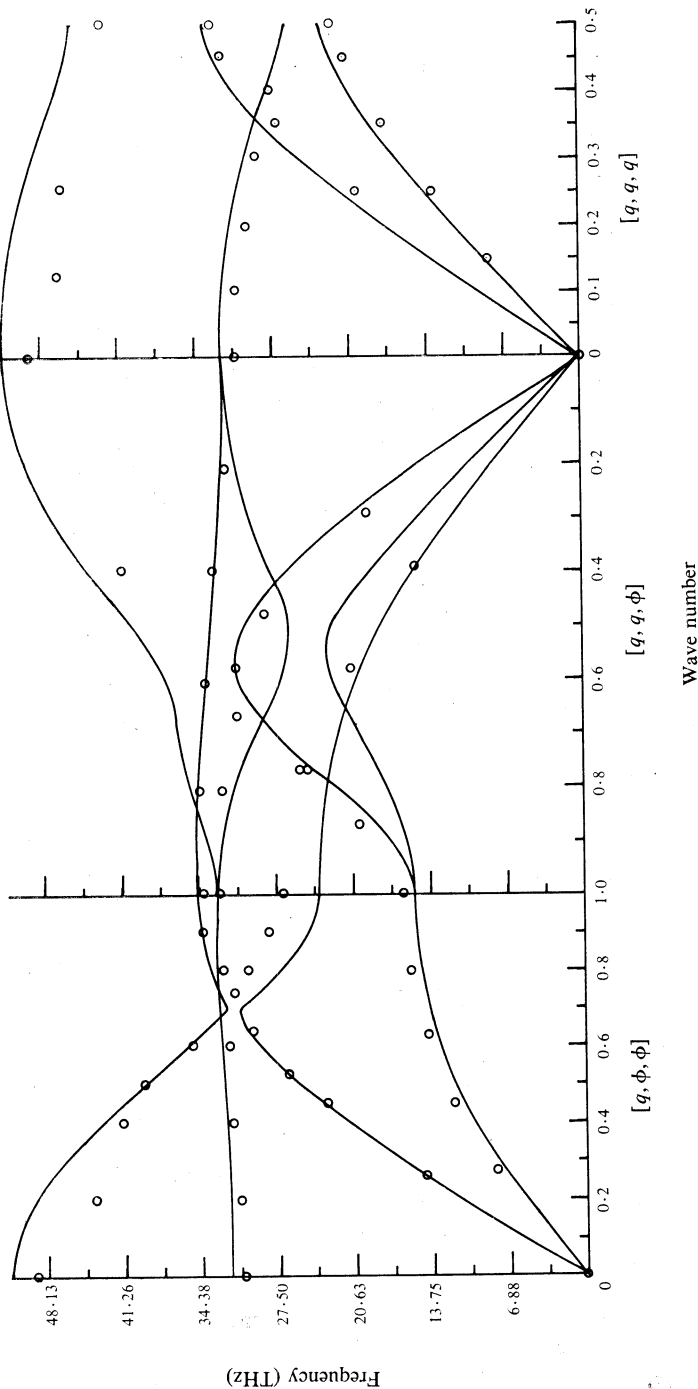
Fig. 1. Phonon dispersion curves for NaCl showing the agreement that can be obtained with experiment. The circles are experimental values due to Schmunk and Winder (1970). To obtain this fit the following parameters were used: $G_- = 600\,\text{eV\,\AA}$, $G_+ = 0\,\text{eV\,\AA}$, $\alpha_- = 3.5\,\text{\AA}^3$ and $\alpha_+ = 0.848\,\text{\AA}^3$. The like-ion deformation interaction was taken to be negligible.

also had some success in fitting experimental results by using the assumption that Hardy and Karo (1979) and others have used of ignoring deformations on positive ions.

Fits to the experimental data were made normally for the [100] phonon dispersion curves (note that elastic constants are independent of the deformation dipoles), and confirmation was obtained by calculations of the [110] and [111] phonon curves. Fitting was done by arbitrarily varying parameters and subjectively assessing the result.

One of our best fits is that shown in Fig. 1. Worst agreement is for the LA mode near the zone boundary in [100] and the LO mode at $q = 0$. Generally it was easier to get better fits in the [110] and [111] directions than in the [100] direction. For calculations in the [100] direction it was generally found that:

(i) the LO mode at $q = 0$ was reduced (from its high rigid-ion value) by increasing both G_- and α_-. The effect of G_+ is opposite to that of G_- at $q = 0$;

(ii) the TO modes at $q = 0$ were reduced by increasing α_- and increased by increasing G_-;

(iii) the 'pinch' between longitudinal modes at about $(0\cdot7, 0, 0)$ is moved inwards by increasing G_-;

(iv) the 'split' between longitudinal modes at $(1, 0, 0)$ is decreased by increasing α_+ relative to α_-, and is increased by decreasing G_+ relative to G_-.

It was found to be difficult to fix both the TO and LO modes near the experimental values at $q = 0$ as well as fitting accurately the 'pinch' area from $(0\cdot7, 0, 0)$ to $(1, 0, 0)$.

Thus, using fewer parameters than are required for a comparable shell model fit, we are able to fit well with the experimental data for the optic modes, near the [100] zone boundary in particular; the fit with LA modes in the same region is not as good. This does not appear to be worse than the result in Fig. 30a (curve DD) of Hardy and Karo (1979).

4. Discussion

With no modifications to the non-Coulomb dynamical matrix we have been able to give a reasonable fit to experimental phonon dispersion curves with a deformation dipole model using just three parameters $(G_-, \alpha_-, \alpha_+)$. We have assumed that like-ion interaction deformations are negligible, and that positive-ion deformations are also negligible.

Our results (Fig. 1) indicate the need for electronic polarizabilities somewhat larger than those given by Pauling (1927) of $\alpha_- = 3\cdot69\,\text{Å}^3$, $\alpha_+ = 0\cdot81\,\text{Å}^3$; Mayer (1933) of $\alpha_- = 3\cdot14\,\text{Å}^3$, $\alpha_+ = 0\cdot18\,\text{Å}^3$; Tessman et al. (1953) of $\alpha_- = 2\cdot974\,\text{Å}^3$, $\alpha_+ = 0\cdot255\,\text{Å}^3$; or Boswarva and Murthy (1981) of $\alpha_- = 3\cdot005\,\text{Å}^3$, $\alpha_+ = 0\cdot285\,\text{Å}^3$. We are close to Pauling's value of α_- but need to have α_+ much larger than any of the quoted values.

We stress that the value of our approach lies in the theoretical justification for our treatment of deformation dipoles, and the small number of parameters we have used to get good agreement with experiment.

As mentioned earlier, our model should also be applicable to other than ionic crystals, provided that $p^{\text{def}}(r)$ for each pair of atoms is known. However, the pair approximation implicit in the above analysis will not be good for non-ionic crystals.

We have assumed that there is a large disparity in size between ions (permitting use of equation 13) and that deformation effects are due solely to the exchange interactions, which also generate the non-Coulomb interaction. We have ignored positive-ion deformations, and deformations due to interactions between like ions. The latter is justified to some extent by the larger separation between nearest like ions compared with nearest unlike ions in the crystal.

We have ignored any relationship between electronic polarizabilities and deformation dipoles, and nor have we given any rigorous argument for the choice of the parameter G_-. Clarification of these aspects is possible, at least in principle, through detailed quantum mechanical calculations of the sort hinted at for instance by MM, but we have not attempted it here.

References

Boswarva, I. M., and Murthy, C. S. N. (1981). *J. Phys. Chem. Solids* **42**, 109–13.

Catlow, C. R. A., Diller, K. M., and Norgett, M. J. (1977). *J. Phys.* C **10**, 1395–1412.

Cochran, W. (1971). *Crit. Rev. Solid State Sci.* **2**, 1–44.

Dick, B. G., and Overhauser, A. W. (1958). *Phys. Rev.* **112**, 90–103.

Fumi, F. G., and Tosi, M. P. (1964). *J. Phys. Chem. Solids* **25**, 31–43.

Hardy, J. R., and Karo, A. M. (1979). 'The Lattice Dynamics and Statics of Alkali Halide Crystals' (Plenum: New York).

Kellermann, E. W. (1940). *Phil. Trans. R. Soc. London* A **238**, 513–48.

Lacey, A. J., and Byers Brown, W. (1974). *Mol. Phys.* **27**, 1013–28.

Lewis, J. T., Lehoczky, A., and Briscoe, C. V. (1967). *Phys. Rev.* **161**, 877–87.

Mahanty, J., and Majumdar, C. K. (1982). *Phys. Rev.* A **26**, 2334–7.

Mayer, J. E. (1933). *J. Chem. Phys.* **1**, 270–9.

Pauling, L. (1927). *Proc. R. Soc. London* A **114**, 181–211.

Raunio, G., Almqvist, L., and Stedman, R. (1969). *Phys. Rev.* **178**, 1496–1501.

Schmunk, R. E., and Winder, D. R. (1970). *J. Phys. Chem. Solids* **31**, 131–41.

Tessman, J. R., Kahn, A. H., and Shockley, W. (1953). *Phys. Rev.* **92**, 890–5.