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IMPROVEMENTS OF INTERATOMIC POTENTIALS IN IONIC CRYSTALS

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Résumé. — Des améliorations des potentiels d'interaction mutuelle pour les cristaux ioniques montrant une violation forte de la relation Cauchy sont présentées. Des déformabilités atomiques et des interactions Van der Waals à corps multiples, sont prises en considération.

Abstract. — Improvements of interatomic potentials for ionic crystals with strong violation of the Cauchy relation are presented. Atomic deformabilities as well as many-body Van der Waals interaction are taken into account. The importance of atomic deformabilities for formation and migration processes of lattice defects is outlined schematically.

1. Introduction. — For an atomistic calculation of lattice defects such as formation energies or activation energies for migration of point defects and dislocations it is necessary to have appropriate interaction potentials. In the case of some sodium- and potassium halides, where the Cauchy relation nearly holds, it is sufficient to take the well established Born-Mayer potential. But if the Cauchy relation is strongly violated, either by

$$c_{12} - c_{44} > 0 \quad (1)$$

for the rubidium-, cesium-, silver- and thallium-halides or by

$$c_{12} - c_{44} < 0 \quad (2)$$

for some lithium halides and alkaline-earth oxides, it is necessary to improve this potential. So we looked for additional terms which are rapidly convergent and not too complicated.

In order to receive such potentials we took their structure, that means their dependence on interatomic distances and angles from quantum mechanical approximations and fitted the corresponding potential parameters to experimental data.

These data are the elastic constants c_{11} , c_{12} , c_{44} , the dielectric constants ϵ_∞ , ϵ_0 , the lattice distance r_0 , the lattice energy U_0 , and some phonon frequencies (transverse and longitudinal modes ω_{0T} , ω_{0L} in the Γ point and the vibrations of the sublattices ω_{1L} , ω_{1T} , ω_{2L} , ω_{2T} in the L point of the Brillouin zone).

Improvements of the potentials were made in two ways :

1) We incorporated atomic deformabilities arising from extensions of the breathing shell model successfully applied already by Sangster [1] and by Bilz *et al.* [2] in order to explain phonon-dispersion relations.

2) We took into account a more exact treatment of the correlation energy (or, in other words, the so-called Van der Waals energy) as carried out by Bauer (private communication) and in [3].

2. Atomic deformabilities. — In order to exceed the rigid ion model in lattice dynamics, being equivalent to two-body central potentials leading to the Cauchy relation

$$c_{12} - c_{44} = 0 \quad (3)$$

some authors [4, 5, 1, 2] took into account inner degrees of freedom of the atoms, e. g. atomic deformabilities. As proposed by Sangster [1], we used the special cases of monopole deformability (MD) leading to $c_{12} - c_{44} < 0$ and quadrupole deformability (QD) resulting in $c_{12} - c_{44} > 0$. The effect of these deformabilities can easily be shown in the simplified case of two dimensions in figure 1 :

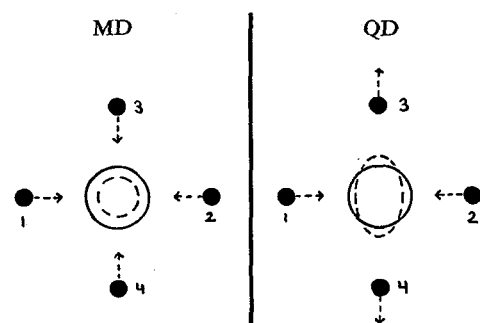


FIG. 1. — Monopole (a) and quadrupole (b) deformabilities.

The atom in the middle is said to be monopole-deformable, if, when the rigid atoms 1 and 2 move towards it, the atom shrinks, leading to an inward movement of the atoms 3 and 4. On the other hand,

an atom is said to be quadrupole-deformable, if, when the rigid atoms 1 and 2 move towards it, the atom is deformed as shown in figure 1*b* leading to an outward movement of the atoms 3 and 4.

The same considerations can be transferred to three dimensions according to the conditions for MD and QD: Constance in atomic shape and volume, respectively. If we suppose that an atom can be deformed only by its nearest neighbours (NN), due to changes in the NN distances, we get new force constants (FC) \hat{C} and \bar{C} between next nearest neighbours and fourth nearest neighbours, respectively, as a result of the atomic deformation leading to the relations:

$$\begin{aligned} \text{MD: } \hat{C} < 0; q = \bar{C}/\hat{C} = 1 \\ \text{QD: } \hat{C} > 0; q = \bar{C}/\hat{C} = -2. \end{aligned} \quad (4)$$

The effect of atomic deformations on the elastic constants can be seen best considering the moduli. So an atomic deformation does not affect the shear modulus $G_2 = c_{44}$, for in this deformation mode no NN distances are changed (see figure 2). The contribution of QD to interatomic forces leads to a decrease of the other shear modulus $G_1 = \frac{1}{2}(c_{11} - c_{12})$ (see figure 3). In the same manner the bulk modulus $K = \frac{1}{3}(c_{11} + 2c_{12})$ is influenced by MD (see figure 4). So we can see that atomic deformabilities only contribute to c_{11} and c_{12} but not to c_{44} . The result is a violation of the Cauchy relation.

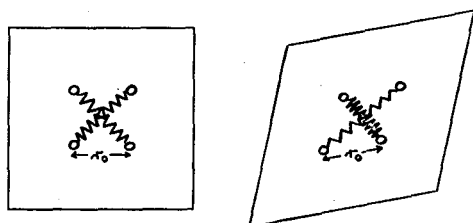


FIG. 2. — No contribution of atomic deformabilities to the shear modulus G_2 .

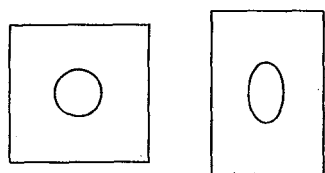


FIG. 3. — Contribution of QD to the shear modulus G_1 .

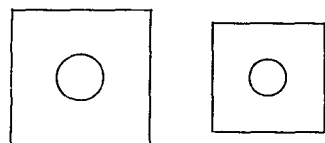


FIG. 4. — Contribution of MD to the bulk modulus K .

The inner degree of freedom, i. e. the degree of atomic deformation can be eliminated from the formalism of lattice theory and expressed by the positions of the neighbouring atoms with the help of adiabatic conditions. This leads to three-body interaction potentials if one kind of ions is supposed to be deformable and the other to be rigid and to additional four-body potentials, if both kinds of ions are supposed to be deformable.

An extension of the ansatz of Sarkar and Sengupta [6] leads to our three-body deformation potential

$$U_{ss}(i, j, k) = \bar{D}_j \exp(-(r_{ij} + r_{jk})/\rho_3) \quad (5)$$

for aligned triples and to

$$U_{ss}(i, j, k) = \hat{D}_j \exp(-(r_{ij} + r_{jk})/\rho_3) \quad (6)$$

for angular triples (see Fig. 5).

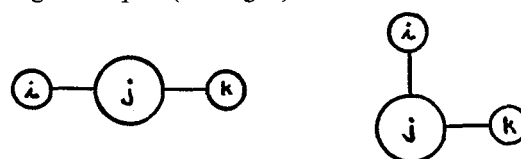


FIG. 5. — Aligned and angular ionic triples.

3. **Van der Waals energy.** — The second improvement of the potentials concerns the correlation energy or the so called Van der Waals (VdW) energy.

The leading term of the VdW energy between two atoms i and j is the dipole-dipole interaction [7]

$$U_{\text{VdW}}^{(2)}(i, j) = -\frac{C_{ij}^{(6)}}{r_{ij}^6}. \quad (7)$$

The next order term is given by the Axilrod-Teller [8] formula obtained in from third order perturbation theory

$$U_{\text{VdW}}^{(3)}(i, j, k) = C_{ijk}^{(9)} \times \frac{1 + 3 \cos \varphi_i \cos \varphi_j \cos \varphi_k}{r_{ij}^3 r_{jk}^3 r_{ki}^3}. \quad (8)$$

This expression is a function of the distances and angles of three atoms yielding contributions to the violation of the Cauchy relation again. The values for $C_{ij}^{(6)}$ calculated by Mayer [7] for alkali halides from ultraviolet absorption are valid only in the asymptotic case of large atomic separations. The actual amount of the two-body VdW⁽²⁾ interaction [3] is at least twice that estimated by Mayer [7] and has been fitted by us to the experimental data mentioned above.

The lattice sums of the three-body VdW⁽³⁾ potential contributing to the lattice energy and to the elastic constants as computed by Bauer *et al.* [9] showed no rapid convergence. So it became desirable to simulate the VdW⁽³⁾ interaction by the rapidly convergent modified Sarkar-Sengupta potential, too.

4. **Conclusions.** — From the fitting procedure we obtained an important result : Although atomic deformabilities have been applied successfully in lattice dynamics it is not sufficient to take into account the pure deformation cases, say either MD or QD. In all ionic crystals investigated so far we found that atomic deformabilities are mixed of MD and QD type and are accompanied by a strong VdW⁽³⁾ interaction in the cases of the silver- and thallium halides.

Thus our potentials give a more detailed scope on the bonding in crystals than lattice dynamics do, for these potentials have not only to yield a set of appropriate FC but they must additionally fit to the lattice energy and they have to obey some further conditions.

Nevertheless, from a heuristic point of view, atomic deformabilities give a physical insight in some special properties of ionic crystals, e. g. the small values of the energies of formation and migration of interstitials in the silver halides. This is shown schematically in figure 6, where the migrating interstitial itself and the neighbouring atoms are deformed in a QD manner which favours the migration process [10].

Many-body VdW interactions do support this trend due to correlations of the electron movements.

We want to emphasize that deformation dependent processes can be described adequately with the help of our improved potentials presented here. Atomistic calculations of the energies of formation and migration of several lattice defects are in progress in the groups of Prof. Granzer and Dr. Bauer.

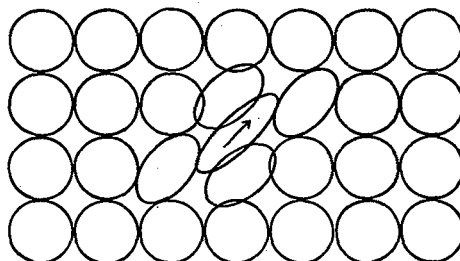


FIG. 6. — Atomic deformabilities favour interstitial migration.

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DISCUSSION

R. J. FRIAUF. — Have your calculations of point defect formation energies progressed to the point where you can provide any simple explanation of the experimental observations. Frenkel defects occur in silver halides, and apparently Schottky defects only also in thallium chloride.

M. BÜCHER. — I think that the introduction of atomic deformabilities together with many-body VdW interaction which is necessary in order to fit the poten-

tials to macroscopic data and which is supported by quantum mechanical considerations can give us a simple explanation of the dominant defect type observed in various ionic crystals. In the case of the silver halides the above mentioned microscopic behaviour of the silver ions is responsible for the Frenkel disorder in these crystals. As to the thallium halides I can't give an explanation for the moment. From atomistic calculations of point defect energies in alkali and silver halides the validity of this prediction will be checked.