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Relaxation of the rocksalt (001) surface: Alkali halides, MgO, and PbS

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We evaluate the static relaxation of the (001) face of rocksalt-structured ionic crystals, using shell models. The results for moderately polarizable compounds, namely, the alkali halides and MgO, are in qualitative agreement with those of earlier calculations but overall somewhat smaller. PbS is treated as an example of highly polarizable substances close to an instability. The results for PbS show a larger and deeper penetrating relaxation than in the case of the alkali halides. Preliminary results for PbTe, which has a large (T-dependent) anion polarizability, show a precursor of a total crystal reconstruction. It is conjectured that in such cases the lowered symmetry at the surface can act as a trigger for a structural phase transition.

I. INTRODUCTION

During the past decade substantial progress was made by Chen *et al.*[1] and Benedek *et al.*[2] in the theoretical and numerical description of the surface dynamics of the unrelaxed (001) faces of the rocksalt-structured alkali halides. More recently, by carrying through substantial improvements in He-surface scattering techniques, Brusdeylins *et al.*[3] have been able to study the surface dynamics of the alkali halides in considerable detail; they were the first to determine complete surface-phonon dispersion curves in certain directions of the Brillouin zone. The overall and, in many cases, detailed good agreement of these theoretical and experimental results seems to indicate that relaxation has a minimal effect on the surface dynamics of the alkali halides. A similar conclusion for MgO had been arrived at by comparing the calculated result of Ref. 1 with the neutron scattering measurements of Rieder and Hörl.[4] In order to understand the reason for this overall agreement, it seemed worthwhile to carry out a systematic study of both the static relaxation of the (001) surfaces of these alkali halides, and of the dynamics of these relaxed surfaces, using the same interaction models for both statics and dynamics. An earlier attempt of this kind by Chen and de Wette[5] seemed to indicate that shell models derived to describe bulk dynamics did not lead to convergent results when used in a surface-relaxation calculation. Since that study was not quite independent (it relied in part on results of Ref. 8), it seemed worthwhile to carry out a new and totally independent relaxation calculation for the rocksalt (001) surface.

An important additional motivation for a systematic study of surface relaxation in conjunction with surface dynamics is the increasing interest in and importance of the surface properties of strongly polarizable systems—e.g., those exhibiting phonon anomalies in the bulk—such as the metal oxides, ferroelectrics, and transition-metal compounds.[6]

An interesting aspect of surface studies in these cases is the stringent test of the particle-interaction models that can result from the lowered symmetry at the surface. For instance, certain cancellations between short-range and Coulomb forces that are present in the bulk are absent at the surface, and the adjustments needed to achieve a new equilibrium configuration may reveal shortcomings in the model which are masked in the bulk as a result of symmetry. Such effects may be particularly important in regimes close to a structural or dynamic instability; in fact, the presence of the surface may trigger the transition to the new state.

However for the alkali halides a number of theoretical studies[5,7–10] during the past 25 years had shown that the relaxations of the (001) faces of these rocksalt-structured crystals are quite small. Unfortunately, there has not been a direct experimental confirmation of these findings, so that the recent surface-dynamical results are the only (indirect) experimental confirmation available at the present time.

In this paper we discuss the determination of relaxed particle positions at and near the (001) face of rocksalt-structured crystals, using particle-interaction models (such as shell models) already available for the bulk to describe electronic polarizabilities, deformation, repulsion, etc. Because of the symmetry of the (001) face the surface unit cell will remain unchanged, i.e., we will encounter relaxation and rumpling, but no reconstruction. The relaxation calculation is carried out for slab-shaped rocksalt-structured crystals bounded by two parallel (001) faces, with no restriction on the thickness of the slab, nor on the number of layers which are allowed to relax.

In Sec. II we present a description of the relaxation calculation, including the changes that need to be made in the treatment of the Coulomb and short-range forces. The method allows for variations in the shell-model parameters as functions of distance from the surface. In Sec. III we present results for the alkali halides and MgO, using bulk shell models, and for PbS as an example of a highly polarizable system close to a structural instability.

II. MODEL AND METHOD

At present a parameter-free description of the surface structure and the dynamical behavior of ionic crystals from first principles is not feasible. We therefore use shell models to determine both the surface structure and the dynamics. The success achieved with shell models in describing bulk dynamics can probably be attributed to the fact that the equations of motion derived from first principles and those obtained with shell models have very similar structures. Shell models take into account short-range overlap forces, long-range Coulomb interactions, and the most important aspects of the displacement-induced deformations of the electronic charge density. The parameters of shell models which are used to describe bulk-phonon dispersion curves of alkali halides have well-defined physical meaning, and are related in a unique way to the elastic constants C_{ij}, the dielectric constants ϵ_0 and ϵ_∞, the polarizabilities α_i, and the reststrahlen frequency $\omega_{\mathrm{TO}}(\Gamma)$.

Surface relaxation is the result of the imbalance of the forces acting on the ionic cores and shells, when the near-surface ions are in their unrelaxed bulk positions. This imbalance can give rise to very large net forces, but very small shifts in the positions can lead to dramatic reductions in the net forces (especially in alkali halides). Since these effects concern a balancing of short-range and Coulomb forces, it is of particular importance that both kinds of forces are evaluated to high accuracy.

The present relaxation calculations were carried out with the bulk shell models, which were used by Chen *et al.*[1] to study the surface dynamics of the unrelaxed rocksalt (001) surfaces of seven alkali halides. It turns out that the relaxations are small and that these shell models are adequate to describe the surface dynamics of the alkali halides. However, for more polarizable substances such as PbS and PbTe the surface introduces a much larger perturbation, and significant modifications or additions (e.g., anharmonic interactions) to the bulk shell models may be needed in order to treat the surface relaxation. We will come back to these points later.

Since the long-range Coulomb interactions and short-range repulsive interactions require different treatment, we consider them separately.

A. Coulomb interactions

Since in predominantly ionic crystals two-body pair potentials (short-range and Coulomb) dominate, there exists no direct mechanism to alter the two-dimensional (2D) symmetry of the surface planes. Hence, surface-related shifts in shell and core positions are restricted to the z direction (relaxation, rumpling) and the symmetry in the x-y planes is maintained, i.e., the 2D unit cell is unchanged. However, cores and shells of ions in the same plane parallel to the surface (i.e., having the same z coordinate in the bulk) will, in principle, relax by different amounts. To allow for this, an extended treatment of the Coulomb interactions is required; it needs to be accurate because of the delicate balance between Coulomb and short-range forces, and computationally fast because of its repeated use in the iteration procedure. Both requirements are fulfilled by a 2D summation procedure based on the Ewald method.

For simplicity, we will refer to the cores and shells of the ions as independent "particles." Thus, the 2D unit cell of the (001) plane of a rocksalt-structured crystal contains four particles (two ions), which are allowed to relax by different amounts. These relaxations will be different for different layers, and for the alkali halides they should rapidly tend to zero with increasing distance from the surface.

The Coulomb forces on a given particle i are obtained as the derivatives of the total Coulomb potential energy of particle i,

$$V_i^c=\sum_{j\neq i}\frac{Q_iQ_j}{|\mathbf{r}_j-\mathbf{r}_i|} ,$$

where the summation is over all other particles (cores and shells) in the lattice; Q_i,Q_j are the charges and $\mathbf{r}_i,\mathbf{r}_j$ the positions of particles i and j.

The Coulomb sums which we have to consider are of two types.

Type 1. A sum describing the Coulomb force in the z direction on a particle in a given layer, due to the particles in a different layer; this is an *inter*layer force. Since in each given layer the particles relax differently, the basic sum is a 2D sum, describing the force due to a plane of like charges (i.e., all the particles of a given kind in a plane properly compensated by a compensating background) on a particle located a z distance of approximately one or a multiple of the interplanar distance r_0 away from it.

Type 2. A sum describing the Coulomb force in the z direction on a particle due to the other particles, which in the unrelaxed case lie in the same plane; i.e., the sum describes an *intra*layer force. The basic sum is a 2D sum, describing the force due to a plane of like charges (with compensating background) on a particle located a z distance away from it, where z is of the order of the relaxation displacements (i.e., $z \ll r_0$).

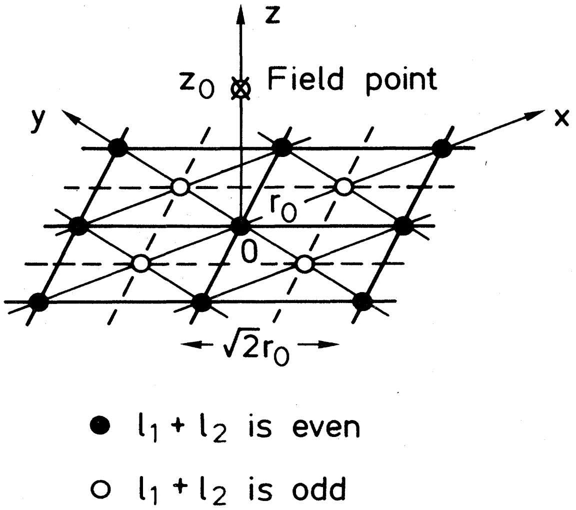

FIG. 1. 2D square lattice with nearest-neighbor distance r_0; lattice points have coordinates $x=l_1r_0$, $y=l_2r_0$. Solid circles indicate the points for which l_1+l_2 is even; open circles indicate the points for which l_1+l_2 is odd.

Of both types of sums we have two kinds, namely one in which the field point lies above the origin of the 2D square lattice, and the other in which the field point lies above the center of a square (cf. Fig. 1). The square lattice that is summed over in each of these sums has lattice distance $\sqrt{2}r_0$, where r_0 is the in-planar nearest-neighbor distance. Using as summation indices l_1 and l_2 (with values $0, \pm 1, \pm 2, \ldots$), such that $l_1 r_0$ and $l_2 r_0$ give the x and y coordinates of a point in the 2D lattice of positive or negative charges, the sum of the first kind is summed over points for which l_1+l_2 is even, whereas for the sum of the second kind l_1+l_2 is odd.

*Type-1 sum (inter*layer sum). This sum describes the z component of the electric field (which, because of symmetry, is the only nonzero component) at a point which lies a distance z_0 away from a planar 2D square lattice of like charges with lattice distance $\sqrt{2}r_0$. We find the electric field as $-\partial/\partial z$ of the potential in the field point z_0, due to such a lattice. However, since the potential itself diverges, we have to subtract the effect of a compensating 2D background in evaluating the potential. The effect of this background is automatically cancelled when the four contributions to the electric field at the field point, resulting from the four different particles associated with this crystal plane, are added, because of the charge neutrality of the unit cell. The z component of the electric field at z_0 due to one of these lattices, when occupied by charges Q, and including the background, is

$$E_z^{e,o} = -Q\frac{\partial}{\partial z}\left[\sum_{\substack{l_1+l_2\\ (\text{even, odd})}} \frac{1}{[(r_0 l_1)^2+(r_0 l_2)^2+z^2]^{1/2}} - \frac{1}{2r_0^2}\int\int \frac{ds_x\,ds_y}{(s_x^2+s_y^2+z^2)^{1/2}}\right]\Bigg|_{z=z_0} . \tag{1}$$

The summation is over l_1 and l_2 with the condition that l_1+l_2 is either even or odd; the density of the uniform compensating background is $-Q(2r_0^2)^{-1}$. In Appendix A we derive for E_x the rapidly converging expressions

$$E_z^{e,o} = \frac{Q\pi}{r_0^2}\sum_{\mu_1,\mu_2}{}' F^{e,o}(\mu_1,\mu_2)\exp\left[-\sqrt{2}\pi\left|\frac{z_0}{r_0}\right|(\mu_1^2+\mu_2^2)^{1/2}\right] \tag{2a}$$

$$= \frac{Q\pi}{2r_0^2}\sum_{\lambda_1,\lambda_2}{}' G^{e,o}(\lambda_1,\lambda_2)\exp\left[-\pi\left|\frac{z_0}{r_0}\right|(\lambda_1^2+\lambda_2^2)^{1/2}\right] . \tag{2b}$$

The sums $\sum'_{\mu_1,\mu_2}$ and $\sum'_{\lambda_1,\lambda_2}$ are both over a 2D square lattice with lattice distance 1; the prime means that the origins ($\mu_1=\mu_2=0$ and $\lambda_1=\lambda_2=0$, respectively) are excluded from the summation. Further,

$$F^e(\mu_1,\mu_2)=1 ,$$
$$F^o(\mu_1,\mu_2)=(-1)^{\mu_1+\mu_2} , \tag{3a}$$

$$G^e(\lambda_1,\lambda_2)=1+(-1)^{\lambda_1+\lambda_2} ,$$
$$G^o(\lambda_1,\lambda_2)=(-1)^{\lambda_1}+(-1)^{\lambda_2} . \tag{3b}$$

The equivalent expressions (2a) and (2b) are both given here, because, while we used (2a) in this relaxation study, the notation of (2b) corresponds to the one used by Chen *et al.*[1] in their surface-dynamical studies.

*Type-2 sum (intra*layer sum). The basic expression is again Eq. (1), but in this case z is the difference of the relaxation displacements of two particles which, in the unrelaxed case, lie in the same plane. Thus z is at least smaller and in most cases much smaller than r_0; for such z values, expressions (2a) and (2b) are not rapidly converging. We follow a different approach.

As indicated above, we have four particles (cores and shells of positive and negative ions) in the 2D unit cell; they are numbered such that 1 and 2 belong to one ion, and 3 and 4 to the other ion. Let these particles have charges Q_i $(i=1,\ldots,4)$ (core and shell charges), and suppose that in a given relaxation iteration they have displacements z_i with respect to the unrelaxed plane. Then the potential at the position of particle 1 is

$$V_1 = \frac{1}{r_0}\sum_{\substack{l_1+l_2\\ (\text{even})}}{}' \left[\frac{Q_1}{(l_1^2+l_2^2)^{1/2}} + \frac{Q_2}{[l_1^2+l_2^2+(z_2-z_1)^2/r_0^2]^{1/2}}\right]$$
$$+\frac{1}{r_0}\sum_{\substack{l_1+l_2\\ (\text{odd})}} \left[\frac{Q_3}{[l_1^2+l_2^2+(z_3-z_1)^2/r_0^2]^{1/2}} + \frac{Q_4}{[l_1^2+l_2^2+(z_4-z_1)^2/r_0^2]^{1/2}}\right] . \tag{4}$$

The first term is the potential at the position 1 due to the other particles 1 in the same plane. This term will not contribute to the electric force on particle 1, but it has to be included in order for V_1 to be finite ($Q_1+Q_2+Q_3+Q_4=0$). In the contributions of both Q_1 and Q_2, we have to exclude $l_1=l_2=0$, for Q_1 for obvious reasons, and for Q_2 because the dipole on the ion, formed by particles 1 and 2, is considered with the short-range interactions. The z component of the electric field at the position for particle 1 is

$$E_{1,z}=-\frac{\partial V_1}{\partial z_1}=-\frac{Q_2}{r_0^2}\sum_{\substack{l_1+l_2\\ \text{(even)}}}{}^{'}\frac{(z_2-z_1)/r_0}{[l_1^2+l_2^2+(z_2-z_1)^2/r_0^2]^{3/2}}-\frac{Q_3}{r_0^2}\sum_{\substack{l_1+l_2\\ \text{(odd)}}}\frac{(z_3-z_1)/r_0}{[l_1^2+l_2^2+(z_3-z_1)^2/r_0^2]^{3/2}}$$
$$-\frac{Q_4}{r_0^2}\sum_{\substack{l_1+l_2\\ \text{(odd)}}}\frac{(z_4-z_1)/r_0}{[l_1^2+l_2^2+(z_4-z_1)^2/r_0^2]^{3/2}} . \tag{5}$$

We see that (5) contains summands of the form $\delta_i/(l_1^2+l_2^2+\delta_i^2)^{3/2}$, where $\delta_i=(z_i-z_1)/r_0$ $(i=2,3,4)$ is always <1 and in most cases $\ll 1$. Because of this we use in (5), the Taylor expansion,

$$\frac{\delta_i}{(l_1^2+l_2^2+\delta_i^2)^{3/2}}=\frac{\delta_i}{(l_1^2+l_2^2)^{3/2}}-\frac{\frac{3}{2}\delta_i^3}{(l_1^2+l_2^2)^{5/2}}+\frac{\frac{15}{8}\delta_i^5}{(l_1^2+l_2^2)^{7/2}}-\frac{\frac{35}{16}\delta_i^7}{(l_1^2+l_2^2)^{9/2}}$$
$$+\frac{\frac{315}{128}\delta_i^9}{(l_1^2+l_2^2)^{11/2}}-\frac{\frac{693}{256}\delta_i^{11}}{(l_1^2+l_2^2)^{13/2}}+\frac{\frac{3003}{1024}\delta_i^{13}}{(l_1^2+l_2^2)^{15/2}}-\cdots . \tag{6}$$

We can now write for (5),

$$E_{1,z}=-\frac{Q_2}{r_0^2}(\delta_2S^e_{3/2}-\tfrac{3}{2}\delta_2^3S^e_{5/2}+\tfrac{15}{8}\delta_2^5S^e_{7/2}-\tfrac{35}{16}\delta_2^7S^e_{9/2}+\tfrac{315}{128}\delta_2^9S^e_{11/2}-\tfrac{693}{256}\delta_2^{11}S^e_{13/2}+\tfrac{3003}{1024}\delta_2^{13}S^e_{15/2}-\cdots)$$
$$-\frac{1}{r_0^2}[(Q_3\delta_3+Q_4\delta_4)S^o_{3/2}-\tfrac{3}{2}(Q_3\delta_3^3+Q_4\delta_4^3)S^o_{5/2}+\tfrac{15}{8}(Q_3\delta_3^5+Q_4\delta_4^5)S^o_{7/2}$$
$$-\tfrac{35}{16}(Q_3\delta_3^7+Q_4\delta_4^7)S^o_{9/2}+\tfrac{315}{128}(Q_3\delta_3^9+Q_4\delta_4^9)S^o_{11/2}$$
$$-\tfrac{693}{256}(Q_3\delta_3^{11}+Q_4\delta_4^{11})S^o_{13/2}+\tfrac{3003}{1024}(Q_3\delta_3^{13}+Q_4\delta_4^{13})S^o_{15/2}-\cdots] , \tag{7}$$

where

$$S_\alpha^{e,0}=\sum_{\substack{l_1+l_2\\ \text{(even, odd)}}}{}^{'}\frac{1}{(l_1^2+l_2^2)^\alpha} . \tag{8}$$

The sums can be evaluated once and for all, so that the expression for $E_{1,z}$ is simply a power expansion in the δ_i's. For small α $(\frac{3}{2},\frac{5}{2})$ the convergence of $S_\alpha^{e,o}$ is rather slow for direct computer summation. In Table I we list values which were obtained with the incomplete gamma-function method of Nijboer and de Wette.[11] We note here that Benson, Balk, and White[7] have discussed the evaluation of these and other 2D lattice sums by essentially the same method. Both sets of results for the same sums $(S_\alpha^e,\ \alpha=\frac{3}{2},\frac{5}{2},\frac{7}{2})$ are in complete agreement.

We now have expressions for the interlayer and intralayer contributions of the electric field at the position of a particle; these, when taken together with the short-range forces, allow us to evaluate the total force on a particle (core or shell) at each step of the relaxation procedure.

B. Short-range interactions

In principle, we consider short-range interactions between (a) the core and shell on the same ion, (b) shell-shell (ss), core-shell (cs), and core-core (cc) interactions between first and second neighbors. Not all of these interactions are taken into account in each case, but interactions (a) and (b) (ss) are always considered.

In alkali halides the intraionic core-shell interaction can usually be described by a potential quadratic in the shell-core displacement,

$$V_{\rm cs}^S=\frac{k_2}{2}w^2 , \tag{9}$$

where $\mathbf{w}=\mathbf{r}_s-\mathbf{r}_c$ is the relative shell-core displacement.

It is customary (cf. Woods *et al.*[12]) to define the constants of interactions (b) and (c) in terms of overlap potentials such as, for example, $V_{\rm ss}(\mathbf{r}_1,\mathbf{r}_2)$, which arises from the overlap of the wave functions of the ions located at the positions $\mathbf{r}_1$ and $\mathbf{r}_2$.

Let us for the moment assume that this potential is a two-body central potential, i.e.,

$$V_{\rm ss}(\mathbf{r}_1,\mathbf{r}_2)=V_{\rm ss}(|\mathbf{r}_1-\mathbf{r}_2|)\equiv V_{\rm ss}(r) . \tag{10}$$

The second derivatives of this potential with respect to the relative displacement $\mathbf{x}=\mathbf{u}_1-\mathbf{u}_2$ are

TABLE I. Values of the 2D lattice sums $S_\alpha^{e,o}$ given in Eq. (8).

α	S_α^e	S_α^o
$\frac{3}{2}$	9.033 622	16.517 32
$\frac{5}{2}$	5.090 258	23.704 59
$\frac{7}{2}$	4.423 118	45.618 75
$\frac{9}{2}$	4.191 268	90.646 30
$\frac{11}{2}$	4.091 587	181.0725
$\frac{13}{2}$	4.044 922	362.0596
$\frac{15}{2}$	4.022 266	724.0857

$$\frac{\partial^2 V_{\rm ss}}{\partial x_i \partial x_j} = \frac{\partial^2 V_{\rm ss}}{\partial r^2}\frac{x_i x_j}{r^2} + \frac{1}{r}\frac{\partial V_{\rm ss}}{\partial r}\left[\delta_{ij} - \frac{x_i x_j}{r^2}\right], \tag{11}$$

where the indices i and j label the Cartesian components.

The longitudinal and transverse force constants $A/2$ and $B/2$ are the second derivatives of the interaction potential taken parallel and perpendicular to the line which connects the interacting ions. For a two-body central potential these force constants are related to the first and second derivatives of the interaction potential by

$$\frac{A}{2}\left[\frac{e}{2r_0^3}\right] = \left[\frac{\partial^2 V}{\partial r^2}\right]_{\parallel}\Bigg|_{r=r_{\rm eq}} = \frac{\partial^2 V}{\partial r^2}\Bigg|_{r=r_{\rm eq}} \tag{12}$$

and

$$\frac{B}{2}\left[\frac{e^2}{2r_0^3}\right] = \left[\frac{\partial^2 V}{\partial r^2}\right]_{\perp}\Bigg|_{r=r_{\rm eq}} = \frac{1}{r_{\rm eq}}\frac{\partial V}{\partial r}\Bigg|_{r=r_{\rm eq}}, \tag{13}$$

where $r_{\rm eq}$ is the equilibrium distance between the interacting ions ($r_{\rm eq} = r_0$ for nearest neighbors and $r_{\rm eq} = \sqrt{2} r_0$ for second neighbors). Thus the coupling constants A and B which are usually determined by a least-squares fit to the measured phonon dispersion curves determine in a unique way the second *and* first derivatives of a two-body central potential. For a more general potential, Eq. (13) is no longer valid. In such a case the transverse force constant B has to be decomposed into a central part $B_{\rm cent}$ for which Eq. (13) still holds and a noncentral part $B_{\rm n\text{-}cent}$,

$$B = B_{\rm cent} + B_{\rm n\text{-}cent} . \tag{14}$$

We use the static equilibrium condition to decompose B into its central and its noncentral parts. The requirement that the derivative of the total potential with respect to the isotropic deformation of the lattice (i.e., with respect to the lattice constant $a = 2r_0$) has to vanish for a given equilibrium crystal structure leads to the relation

$$\frac{1}{r_0}\frac{\partial V^{+-}}{\partial r}\Bigg|_{r=r_0} + 2\frac{1}{\sqrt{2}r_0}\frac{\partial V^{++}}{\partial r}\Bigg|_{r=\sqrt{2}r_0} + 2\frac{1}{\sqrt{2}r_0}\frac{\partial V^{--}}{\partial r}\Bigg|_{r=\sqrt{2}r_0} = -\frac{1}{3}\left[\frac{e^2}{2r_0^3}\right]\alpha_M Z^2 , \tag{15}$$

where α_M is the Madelung constant and Z is the ionic charge. In Eq. (15) interactions up to second-nearest neighbors have been taken into account. Substituting Eq. (13) into Eq. (15) and keeping in mind that the central-potential part of the transverse force constant is now called $B_{\rm cent}$ yields

$$B^{+-}_{\rm cent} + 2B^{++}_{\rm cent} + 2B^{--}_{\rm cent} = -\tfrac{2}{3}\alpha_M Z^2 . \tag{16}$$

We note (cf. Table II) that the second-neighbor force constants B^{++} and B^{--} are roughly an order of magnitude smaller than the nearest-neighbor force constants B^{+-}. We will therefore only make a very small error if we assume that the second-neighbor interactions are purely central, i.e., $B^{++}_{\rm cent} = B^{++}$ and $B^{--}_{\rm cent} = B^{--}$, where B^{++} and B^{--} are the transverse force constants obtained from shell-model fits to the measured phonon dispersion curves. We can now determine $B^{+-}_{\rm cent}$ from Eq. (16) and calculate the noncentral part according to Eq. (14).

In order to carry out the relaxation calculation we need to know the short-range forces, not only at the static equilibrium positions, but also as a function of the interparticle distances, i.e., we must determine the short-range potentials of which they are first derivatives. The shell-model parameters are usually obtained from a fit to the phonon dispersion curves, which are measured under specific thermodynamic conditions, i.e., at a given density. Thus, the shell model gives us the second derivatives of a yet unknown potential at one specific density, while we need the first derivatives of that potential as functions of density.

For the ionic crystals with rocksalt structure studied in this paper, we approximate the short-range potentials by Born-Mayer potentials of the form

$$V(r) = a\exp(-br) . \tag{17}$$

The potential parameters a and b of these two-body central potentials can be obtained from the force constants A and $B_{\rm cent}$ using Eqs. (12) and (13) [in Eq. (13), B has to be replaced by $B_{\rm cent}$]. Having determined the Born-Mayer potentials $V^{+}(r)$, $V^{++}(r)$, and $V^{--}(r)$, we have the necessary tools to calculate the short-range forces as functions of the interionic distances. At this stage we would like to stress the following points.

(1) The procedure outlined above implies that in our relaxation calculation we neglect all noncentral interactions; the reason is that no potential for such interactions has been given up until now.

(2) If we had used the total B^{+-} instead of $B^{+-}_{\rm cent}$ to construct a nearest-neighbor Born-Mayer potential V^{+-}, then the crystal (at its bulk nearest-neighbor distance) would *not* have been in an equilibrium configuration compatible with this potential. This would mean that the existing equilibrium would somehow have to be maintained by an external pressure (positive or negative). This would have no special consequences as long as only the bulk is considered, because as a result of bulk symmetry the forces on a particle cancel each other in the bulk. However, the presence of a surface destroys the bulk symmetry, and the incompability of the bulk lattice distance with the nearest-neighbor short-range potential would manifest itself. In particular, if no external pressure would be applied to maintain the bulk nearest-neighbor distance in the interior of the crystal, the crystal would attempt to find a new bulk nearest-neighbor distance as soon as it is allowed to relax, which would give rise to a nonconverging relaxation, i.e., to relaxation shifts which do not diminish away from the surface. (This, in fact, appears to have been the cause of the nonconverging relaxation reported in Ref. 5.)

(3) We can summarize by reiterating that we have avoided these unphysical effects by determining the nearest-neighbor Born-Mayer potential in a way which is consistent with the bulk equilibrium condition (14). The noncentral force constant $B^{+-}_{\rm n\text{-}cent}$ cannot be further used, since there is no potential known for it, and hence no way to determine the forces resulting from it. The magnitude

of $B^{+-}_{\text{n-cent}}$ [as given by (16)] as compared to B^{+-}_{cent} is a measure for the error which is made in this way.

C. Relaxation procedure

Starting from the unrelaxed bulk positions, the relaxed positions of the cores and shells (particles) in the slab are found as those positions for which the total forces on the particle vanish. These final relaxed positions are obtained as follows: The total force in the z direction on a particle i, F_z^i, is a function of the positions $\mathbf{r}_j$ of all the other particles in the slab. We use the expansion

$$F_z^i(\{\mathbf{r}_j\})=F_z^i(\{\mathbf{r}_j^0\})+\sum_j\left[\frac{\partial F_z^i}{\partial z_j}\right]_0 z_j,\quad \mathbf{r}_j=\mathbf{r}_j^0+\mathbf{k}z_j \tag{18}$$

where the set $\{\mathbf{r}_j^0\}$ gives the starting positions of the particles in each step of the iteration ($\mathbf{k}$ is the unit vector in the z direction). We can write (18) in matrix notation as follows:

$$\mathbf{F}_z(\{\mathbf{r}_j\})=\mathbf{F}_z(\{\mathbf{r}_j^0\})+\underline{\mathbf{D}}\mathbf{z}\ . \tag{19}$$

$\mathbf{F}_z$ has the dimension of 4 times the number of layers in the slab that are allowed to relax: there are two ions per layer in the unit cell, and two particles (core, shell) per ion. We try to arrive at a set of positions $\{\mathbf{r}_j\}$ such that $\mathbf{F}_z(\{\mathbf{r}_j\})=0$. Thus the displacement vector $\mathbf{z}$ leading to this configuration follows from

$$\mathbf{z}=-\underline{\mathbf{D}}^{-1}\mathbf{F}_z(\{\mathbf{r}_j^0\})\ . \tag{20}$$

Since (19) is a truncated expansion, we need an iteration procedure to approach the configuration $\{\mathbf{r}_j\}$ for which $\mathbf{F}_z$ vanishes. However, from a numerical point of view it is not worthwhile to go beyond the linear term in (19), and, in any event, for the weakly polarizable systems like the alkali halides and MgO, about four iteration steps are sufficient to obtain the relaxed configuration. The latter is considered to have been reached when the forces F_z^i are of the order or smaller than 10^{-5} in units in which B^{+-}_{cent} ranges between 0.5 and 10. In such a configuration the effect of any residual unbalanced forces on the dynamics of the slab will be totally negligible.

The question as to how many layers should be involved in a relaxation calculation is determined by the following consideration: It is found that the innermost layer that is relaxed, i.e., the layer adjacent to the bulk, always has a relaxation that adjusts itself to the unrelaxed bulk. This effect should not influence the relaxation of the outermost layer, which it would if too few layers were allowed to relax. Thus, the criterion that a sufficient number of layers are allowed to relax is that the top-layer relaxation is not significantly changed when an additional layer is involved in the relaxation. In view of this consideration, a one-layer relaxation is never sufficient to obtain a realistic result.

The relaxation procedure of strongly polarizable substances such as PbTe is considerably more complex. Because of the incipient instability, one cannot relax all layers simultaneously, but has to start with relaxing one single layer, then use the relaxed configuration of this one layer as the starting configuration for the relaxation of two layers, and so forth. The total number of layers to be involved has to be carefully judged. For instance, for a given number of layers, one may obtain what appears as a converging (diminishing) relaxation, but then, when adding more layers, the relaxation shifts may be large again. Involving still more layers, this whole pattern may repeat itself. What one may be seeing in such a case is a precursor of a structural transition starting at the surface, but which is not able to persist into the bulk, because the thermodynamic conditions for a bulk transition are almost, but not fully, satisfied.

The occurrence of these near-transition-like configurational changes emphasizes the great importance of a very carefully executed relaxation calculation. In this connection the procedure of accurately evaluating the forces (i.e., the gradients of the total multidimensional potential-energy function) at each step of the iteration is a far more sensitive procedure than seeking a minimum of the potential energy by a finite-step procedure. Since in the latter case one would be seeking the minimum of a (in general) shallow potential-energy valley, the step size cannot be made too small, or the potential differences become of the order of the rounding errors of the computer. But for an adequate step size the potential gradients are not sufficiently accurately known, so that one runs the risk of continually missing the true minimum of the function. Thus, in general, in a problem in which the forces can be accurately evaluated, as in the present case, it is a far better procedure to seek a configuration of vanishing forces than to minimize the potential-energy function. It is also important to continue the iterations until the residual forces have fallen below a specified limit. In this connection we consider a one-step determination of the relaxed positions, as, for instance, was carried out by Welton-Cook and Prutton,[9] as rather inadequate.

We will see that the relaxations obtained in this work are in most cases smaller than those obtained in other relaxation studies. This may, in part, be the result of the very sensitive relaxation procedure employed here.

III. RESULTS AND DISCUSSION

A. Alkali halides and magnesium oxide

In Table II we list the equilibrium configurations for four-layer relaxation calculations ($n=1,\ldots,4$). The quantities z_c^+, z_s^+, z_c^-, and z_s^- are, respectively, the shifts the z direction of the positive core and shell, and the negative core and shell from their bulk positions, in units of the bulk nearest-neighbor distance r_0 (outward shifts are positive, inward shifts negative). Since in all cases the positive and negative cores relax by different amounts, the relaxed surface is *rumpled*. The quantity $\frac{1}{2}(z_c^+ + z_c^-)$ gives the average relaxation of the ions in the planar unit cell, and hence it is a measure of the average shift of the plane; $z_c^+ - z_c^-$ is the difference in relaxation of the positive and negative cores, and hence it is a measure of the rumpling. Furthermore,

$$\mu_+ = Y_+(z_s^+ - z_c^+),\quad \mu_- = Y_-(z_s^- - z_c^-)$$

are the surface-induced dipole moments of the positive

TABLE II. Equilibrium configurations of cores and shells in the surface region at the (001) face of alkali halide crystals and magnesium oxide. The column headings are defined in the text.

Layer	z_c^+	z_s^+	z_c^-	z_s^-	$\frac{1}{2}(z_c^+ + z_c^-)$	$z_c^+ - z_c^-$	μ^+	μ^-	$\frac{1}{2}(z_c^+ + z_c^-)_n - \frac{1}{2}(z_c^+ + z_c^-)_{n+1}$
					LiD				
1	0.009 83	0.009 83	−0.021 16	−0.027 16	−0.005 66	0.030 99	0	0.007 14	−0.006 43
2	−0.003 69	−0.003 69	0.005 23	0.004 07	0.000 77	−0.008 92	0	0.001 38	−0.000 89
3	0.000 93	0.000 93	−0.001 17	−0.000 74	−0.000 12	0.002 10	0	−0.000 52	−0.000 15
4	−0.000 20	−0.000 20	0.000 25	0.000 14	0.000 03	−0.000 45	0	−0.000 12	
					LiF				
1	−0.022 73	−0.023 41	0.008 01	−0.002 00	−0.007 36	−0.030 74	−0.000 94	0.018 34	−0.008 93
2	0.005 13	0.005 17	−0.002 00	−0.000 58	0.001 57	0.007 13	0.000 06	−0.002 60	0.001 87
3	−0.001 04	−0.001 05	0.000 45	0.000 18	−0.000 30	−0.001 49	0.000 00	0.000 50	−0.000 36
4	0.000 21	0.000 21	−0.000 09	−0.000 04	0.000 06	0.000 30	0.000 00	−0.000 09	
					NaF				
1	−0.008 18	−0.007 37	−0.002 53	−0.007 70	−0.005 26	−0.005 65	−0.006 92	0.009 73	−0.005 81
2	0.000 60	0.000 53	0.000 31	0.000 72	0.000 45	0.000 28	0.000 59	−0.000 77	0.000 49
3	−0.000 03	−0.000 02	−0.000 05	−0.000 08	−0.000 04	0.000 02	0.000 08	0.000 06	−0.000 04
4	0.000 00	0.000 00	0.000 01	0.000 01	0.000 00	−0.000 01	0.000 00	0.000 00	
					NaCl				
1	−0.022 65	−0.024 24	0.011 08	−0.001 15	−0.005 79	−0.033 73	−0.004 16	0.030 43	−0.007 54
2	0.007 61	0.007 73	−0.004 11	−0.001 75	0.001 75	0.011 72	0.000 31	−0.005 87	0.002 17
3	−0.002 20	−0.002 20	0.001 35	0.000 74	−0.000 42	−0.003 55	0.000 00	0.001 54	−0.000 54
4	0.000 63	0.000 62	−0.000 38	−0.000 21	0.000 12	0.001 00	0.000 00	−0.000 42	
					NaCl				
1	−0.020 49	−0.020 86	0.011 18	0.002 90	−0.004 66	−0.031 67	−0.000 39	0.025 08	−0.006 01
2	0.006 75	0.006 77	−0.004 05	−0.002 56	0.001 35	0.010 79	0.000 02	−0.004 48	0.001 66
3	−0.001 93	−0.001 93	0.001 32	0.000 92	−0.000 31	−0.003 25	0.000 00	0.001 21	−0.000 40
4	0.000 55	0.000 55	−0.000 36	−0.000 26	0.000 09	0.000 91	0.000 00	−0.000 33	
					NaBr				
1	−0.031 17	−0.029 67	0.015 31	0.004 50	−0.007 93	−0.046 48	0.001 26	0.041 90	−0.010 61
2	0.012 13	0.011 99	−0.006 77	−0.004 05	0.002 68	0.018 90	−0.000 27	−0.010 54	0.003 35
3	−0.004 04	−0.004 02	0.002 70	0.001 80	−0.000 67	−0.006 74	0.000 02	0.003 49	−0.000 91
4	0.001 35	0.001 35	−0.000 86	−0.000 58	0.000 24	0.002 21	0.000 00	−0.001 12	
					NaI				
1	0.025 93	−0.031 25	0.012 84	0.002 29	−0.006 54	−0.038 77	−0.011 66	0.041 69	−0.009 81
2	0.012 28	0.013 08	−0.005 74	−0.001 90	0.003 27	0.018 02	0.001 75	−0.011 22	0.004 09
3	−0.004 00	−0.004 15	0.002 35	0.001 46	−0.000 82	−0.006 36	−0.000 33	0.003 52	−0.001 11
4	0.001 32	0.001 35	−0.000 74	−0.000 48	0.000 29	0.002 06	0.000 07	−0.001 08	

TABLE II. (*Continued*).

Layer	z_c^+	z_s^+	z_c^-	z_s^-	$\frac{1}{2}(z_c^+ + z_c^-)$	$z_c^+ - z_c^-$	μ^+	μ^-	$\frac{1}{2}(z_c^+ + z_c^-)_n - \frac{1}{2}(z_c^+ + z_c^-)_{n+1}$
					KF				
1	0.01060	0.00585	−0.02388	−0.02531	−0.00664	0.03448	−0.02175	0.00362	−0.00823
2	−0.00411	−0.00327	0.00729	0.00732	0.00150	−0.01141	0.00389	−0.00008	0.00193
3	0.00129	0.00109	−0.00197	−0.00194	−0.00034	0.00326	−0.00096	−0.00005	−0.00043
4	−0.00034	−0.00029	0.00052	0.00052	0.00009	−0.00087	0.00023	0.00003	
					KCl				
1	0.01449	0.01608	−0.02529	−0.02705	−0.00540	0.03978	−0.02131	0.00428	−0.00725
2	−0.00628	−0.00661	0.00997	0.00992	0.00185	−0.01625	0.00453	0.00012	0.00224
3	0.00234	0.00234	−0.00312	−0.00305	−0.00039	0.00546	−0.00133	−0.00017	−0.00052
4	−0.00070	−0.00073	0.00097	0.00094	0.00013	−0.00167	0.00040	0.00007	
					KBr				
1	−0.00307	−0.00806	−0.00437	−0.01050	−0.00372	0.00130	−0.01596	0.02024	−0.00422
2	0.00024	0.00086	0.00077	0.00147	0.00050	−0.00053	0.00198	−0.00231	0.00056
3	0.00003	−0.00005	−0.00015	−0.00022	−0.00006	0.00018	−0.00026	0.00023	−0.00007
4	−0.00002	−0.00001	0.00004	0.00004	0.00001	−0.00006	0.00003	−0.00003	
					KI				
1	−0.00845	−0.01318	0.00076	−0.00514	−0.00385	−0.00921	−0.01298	0.02709	0.00460
2	0.00353	0.00405	−0.00204	−0.00102	0.00075	0.00557	0.00143	−0.00464	0.00089
3	−0.00136	−0.00138	0.00107	0.00082	−0.00014	−0.00243	−0.00008	0.00115	−0.00018
4	0.00048	0.00047	−0.00040	−0.00033	0.00004	0.00088	−0.00003	−0.00032	
					RbF				
1	0.00115	0.00046	−0.02343	−0.02771	−0.01114	0.02458	−0.02877	0.01077	−0.01431
2	−0.00321	−0.00305	0.00955	0.01003	0.00317	−0.01277	0.00709	−0.00118	0.00397
3	0.00157	0.00152	−0.00318	−0.00320	−0.00080	0.00475	−0.00208	0.00005	−0.00105
4	−0.00053	−0.00051	0.00103	0.00103	0.00025	−0.00156	0.00042	0.00003	
					RbCl				
1	−0.00799	−0.00220	−0.00517	−0.00924	−0.00658	−0.00282	−0.00858	0.01351	−0.00748
2	0.00010	−0.00066	0.00170	0.00207	0.00090	−0.00160	0.00113	−0.00123	0.00103
3	0.00026	0.00038	−0.00052	−0.00053	−0.00013	0.00078	−0.00018	0.00007	−0.00016
4	−0.00010	−0.00013	0.00015	0.00015	0.00003	−0.00026	0.00003	0.00003	
					RbBr				
1	0.02772	0.02854	−0.02968	−0.03049	−0.00098	0.05740	−0.03051	0.00145	−0.00463
2	−0.00845	−0.00866	0.01575	0.01570	0.00365	−0.02419	0.00781	0.00007	0.00422
3	0.00345	0.00352	−0.00460	−0.00458	−0.00057	0.00805	−0.00260	−0.00004	−0.00084
4	−0.00104	−0.00106	0.00157	0.00156	0.00027	−0.00261	0.00074	0.00002	

TABLE II. (*Continued*).

Layer	z_c^+	z_s^+	z_c^-	z_s^-	$\frac{1}{2}(z_c^+ + z_c^-)$	$z_c^+ - z_c^-$	μ^+	μ^-	$\frac{1}{2}(z_c^+ + z_c^-)_n - \frac{1}{2}(z_c^+ + z_c^-)_{n+1}$
					RbI				
1	−0.056 11	−0.058 08	0.056 05	0.051 72	−0.000 03	−0.112 16	−0.005 65	0.067 47	−0.012 04
2	0.042 42	0.042 48	−0.018 39	−0.016 62	0.012 01	0.060 80	0.000 17	−0.027 52	0.010 15
3	−0.013 71	−0.013 81	0.009 99	0.009 25	−0.001 86	−0.023 70	−0.000 29	0.011 50	−0.000 57
4	0.005 98	0.005 98	−0.003 40	−0.003 13	0.001 29	0.009 39	0.000 00	−0.004 20	
					MgO				
1	−0.017 88	−0.017 88	0.006 51	−0.012 62	−0.005 69	−0.024 39	0	0.058 16	−0.006 39
2	0.003 22	0.003 22	−0.001 82	0.006 8	0.000 70	0.005 04	0	−0.007 60	0.000 77
3	−0.000 63	−0.000 63	0.000 49	0.000 07	−0.000 07	−0.001 12	0	0.001 28	−0.000 08
4	0.000 13	0.000 13	−0.000 11	−0.000 03	0.000 01	0.000 24	0	−0.000 24	
					PbS				
1	−0.015 85	−0.058 12	−0.037 67	−0.117 55	−0.026 76	0.021 82	−0.300 92	0.244 72	−0.079 09
2	0.039 00	0.075 26	0.065 66	0.132 37	0.052 33	−0.026 66	0.258 13	−0.204 40	0.072 40
3	−0.012 15	−0.034 18	−0.027 98	−0.068 05	−0.020 07	0.015 83	−0.156 76	0.122 78	−0.044 67
4	0.016 10	0.033 77	0.031 69	0.062 98	0.023 90	−0.015 59	0.125 79	−0.095 84	0.036 17
5	−0.007 35	−0.019 08	−0.017 18	−0.037 98	−0.012 27	0.009 83	−0.083 51	0.063 73	−0.023 68
6	0.007 25	0.016 16	0.015 57	0.031 12	0.011 41	−0.008 32	0.063 43	−0.047 61	0.018 03
7	−0.003 93	−0.009 91	−0.009 30	−0.019 79	−0.006 62	0.005 37	−0.042 57	0.032 14	−0.011 86
8	0.003 25	0.007 44	0.007 23	0.014 51	0.005 24	−0.003 98	0.029 83	−0.022 31	0.008 05
9	−0.001 65	−0.004 18	−0.003 97	−0.008 38	−0.002 81	0.002 32	−0.017 94	0.013 51	−0.004 42
10	0.001 03	0.002 28	0.002 19	0.004 37	0.001 61	−0.001 16	0.008 90	−0.006 68	

TABLE III. Shell-model parameters for the alkali halides and MgO from various sources. (RT denotes room temperature.)

	Units[a]	LiD[b]	LiF[c]	NaF[d]	NaCl[e,f]		NaBr[g]	NaI[h]
A^{+-}	$e^2/2v$	6.146	7.739	9.26	10.264	9.77	10.91	9.94
B^{+-}	$e^2/2v$	−0.748	−0.874	−0.77	−0.971	(−0.86)	−0.88	(−0.8668)
$B^{+-}_{\text{n-cent}}$	$e^2/2v$	(0.656)	(0.2122)	(0.148)	(0.115)	0.055	(0.194)	−0.026
A^{++}	$e^2/2v$	0	−0.317	0	−0.427	−0.006	0	0
B^{++}	$e^2/2v$	0	0.051	0	0.022	0.004	0	0
A^{--}	$e^2/2v$	−0.400	1.030	0.34	0.597	0.56	0	0.618
B^{--}	$e^2/2v$	0.253	−0.056	−0.02	−0.025	−0.006	0	−0.041
Z	e	0.878	0.970	0.907	0.968	0.890	0.96	0.890
α_+	Å^3	0	0.1011	0.27	0.493	0.18	0.64	1.98
d_+	e	0	−0.027	0.01	−0.035	−0.031	−0.13	−0.112
α_-	Å^3	1.566	0.7292	0.70	2.601	2.35	3.62	4.34
d_-	e	0.363	0.1460	0.116	0.194	0.131	0.16	0.136
r_0	Å	2.035	2.013	2.312	2.820	2.80	2.989	3.211
T	K	300	290	RT	RT	80	295	100
Derived quantities								
X_+	e	0	−0.406	9.343	−1.647	−0.175	0.117	−1.301
Y_+	e	0.878	1.376	−8.436	2.615	1.065	0.843	2.191
X_-	e	0.312	0.864	0.979	1.520	2.400	2.916	3.062
Y_-	e	−1.190	−1.834	−1.886	−2.488	−3.290	−3.876	−3.952
k_+	e^2/v	∞	299.27	6505.2	613.50	268.19	50.215	152.30
k_-	e^2/v	10.590	69.276	117.765	98.406	193.91	212.52	230.30

[a] Here, $v=2r_0^3$ is the volume of the bulk unit cell; r_0 is the bulk nearest-neighbor distance.

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and negative ions in the successive layers. Finally, we list the average fractional change in distance between the nth and $(n+1)$th layer,

$$d_n=\tfrac{1}{2}(z_c^+ + z_c^-)_n - \tfrac{1}{2}(z_c^+ + z_c^-)_{n+1}\ .$$

Two observations are immediately obvious from these results: First, the relaxations are quite small, at most a few percent of the interlayer distance in the outer layer ($n=1$), and second, the relaxations diminish rapidly with increasing distance from the surface. Therefore, restricting the calculation to four surface planes is completely sufficient in alkali halides and MgO. In fact, if we allow a fifth layer to relax, nothing happens, i.e., the fifth layer does not shift and the relaxations in the first four layers remain the same.

In studying Table II, we note the following systematic features.

(1) Looking just at the outer layer, the ion with smaller polarizability relaxes inward from the ion with the larger polarizability. Accordingly, LiF, NaF, NaCl, NaBr, NaI, KI, and RbI, for which $\alpha_- > \alpha_+$, all show *negative rumple*, i.e., $(z_+^c - z_-^c) < 0$. MgO also falls into this category, although the shell model used in this work yields a larger polarizability for Mg^{2+} than for O^{2-}; this is an unphysical aspect of the model. (A typical relaxation pattern with negative rumple is shown in Fig. 2.)

(2) According to this same principle, KF, KCl, RbF, and RbBr, for which $\alpha_+ > \alpha_-$, all exhibit *positive rumple*, i.e., $(z_+^c - z_-^c) > 0$. However, we draw attention to the fact that the shell models of KCl, RbF, and RbB all have rather large cation-shell charges. In these models the core and shell charges of the positive ion mimic the effects of overlap polarization; they do not describe the genuine positive-ion polarizabilities. In fact, because of changes in overlap effects at the surface, a properly surface-adapted shell model should contain corresponding changes in these parameters for ions near the surface. However, for the present calculation no such changes have been made. It is, therefore, quite possible that the positive rumple which we are seeing in these cases is a model effect.

(3) The exceptions to the general rule of points (1) and (2) are LiCl and KBr, for which $\alpha_- > \alpha_+$, but which both show positive rumple. These cases indicate that the rumpling is not solely a function of the ratio of the polariza-

TABLE III. (*Continued*).

KF[i]	KCl[f]	KBr[h]	KI[j]	RbF[f]	RbCl[f]	RbBr[k]	RbI[l]	MgO[m]
10.760	11.17	13.15	13.4	12.31	12.01	12.00	13.82	29.13
−1.130	(−0.784)	(−1.227)	−1.0	(−1.416)	(−0.827)	(−0.634)	(−0.938)	−3.51
(0.008)	0.011	−0.034	(0.066)	−0.15	−0.20	−0.195	−0.096	(1.142)
0.317	0.27	0	−0.16	0.02	0.36	0.50	−0.28	0
−0.054	−0.074	0	−0.01	0.0003	−0.04	−0.18	0.19	0
−0.247	0.15	−0.399	−0.29	−0.17	0.31	0.11	0.64	−1.353
0.085	0.08	0.054	0.05	0.050	−0.01	0.036	−0.21	0.256
0.961	0.82	0.965	0.92	1.00	0.79	0.79	0.87	1.885
1.233	1.61	2.12	2.28	1.54	0.66	3.04	2.29	0
−0.060	0.019	−0.101	−0.11	−0.008	0.066	0.011	−0.099	0
0.455	0.99	3.05	4.51	1.15	2.31	0.56	5.64	(1.760)
0.040	0.064	0.141	0.13	0.099	0.103	0.042	0.045	(0.685)
2.672	3.126	3.274	3.505	2.805	3.27	3.416	3.629	2.106
RT	80	90	90	80	80	80	80	RT
Derived quantities								
−3.617	14.137	−2.234	−1.824	−40.338	2.271	37.992	2.020	0
4.578	−13.317	3.199	2.744	41.338	−1.481	−37.202	2.890	(1.885)
1.573	1.611	2.336	3.672	1.494	2.531	1.005	14.792	(1.155)
−2.534	−2.431	−3.301	−4.592	−2.494	−3.321	−1.795	−15.662	−3.04
640.07	6719.81	328.30	272.96	48 920.0	222.00	36 284.0	336.79	∞
530.01	355.10	239.80	391.32	229.36	323.56	447.89	4145.14	75.97

bilities but is, to some extent, determined by other model properties as well. Also, in the case of LiD, the shell model is unphysical in that it assigns zero polarizability to the Li ion, so that the rule linking the rumpling to the ratio of the polarizabilities is not really applicable in this case. On the other hand, in KBr the (anomalous) positive rumple is very small, so this case is not a very significant exception to the rule.

(4) The rumple of the top layer is repeated in lower layers, but with decreasing amplitude and alternating sign. That is, if in the top layer the positive ion is relaxed inward, then in the next layer the negative ion underneath it is also relaxed inward, etc. The rumpling dies out in three or four layers.

(5) The average layer shift $\frac{1}{2}(z_c^+ + z_c^-)$ is negative in the top layer and alternates in sign in successive layers, i.e., it is inward for the first and third layers and outward for the second and fourth layers; the exception is RbI, where the pattern is reversed.

These regularities in the relaxation results are the most pronounced ones. To look for further, less obvious, regularities is not very useful, since in any particular case the details in the relaxation are the result of the interplay of the various model parameters in that particular case.

We have considered two shell models for NaCl (cf. Table III); the first, because it is the model used by Chen *et al.*[1] in their dynamics calculations, and the second because it is physically the better model: it has a more realistic anion polarizability and negligible overlap between cation second neighbors. The relaxation results for the two models are in good agreement, except for the shell shifts of the Cl$^-$, which, although small in both cases, differ by a factor of 2; we attribute this to the large difference in anion polarizability between the two models.

We now compare the present results with those of earlier calculations. We first mention the relaxation calculation of Chen and de Wette[5] for NaCl, NaI, and MgO, using the same shell models as were used here. These authors erroneously used the total B^{+-} to construct the Born-Mayer potential V^{+-}, with the result that the bulk equilibrium distance is not compatible with this potential (cf. Sec. II). This gave rise to nonconverging average fractional interlayer shifts d_n and was the basis of the erroneous conclusion that bulk dynamic shell models are unable to describe static relaxation phenomena in a consistent fashion.

The first and most extensive relaxation calculations of alkali halides using shell models have been carried out by Benson and Claxton.[8] There is qualitative overall agreement in the magnitude of the relaxations and their de-

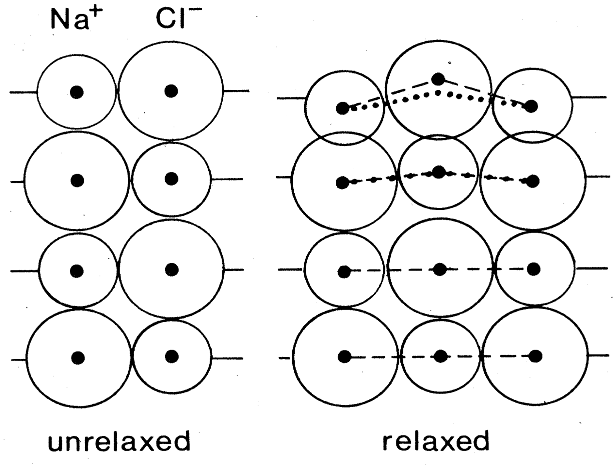

FIG. 2. Typical relaxation pattern for alkali halides with negative rumple (NaCl). The vertical relaxation is enhanced by a factor of 10. The dashed line indicates the warping of the core positions, the dotted line that of the shell positions.

crease away from the surface between our results and those of Ref. 8, although, in general, the relaxations of Ref. 8 are somewhat larger. However, this lack of agreement in detail is not surprising. The present calculations are based on shell models which are designed to fit bulk-phonon dispersion curves over the entire Brillouin zone, and hence the models have a certain internal consistency. The models of Ref. 8 contain model parameters which were taken from a variety of different sources, some dating back as far as 1933. Moreover, the models of Ref. 8 include van der Waals interactions, which we have not taken into account.[14] In view of these differences, the overall qualitative agreement between these sets of calculations is comforting. At the same time, the differences in detail point to the sensitivity of the results to the details of the interaction models.

Martin and Bilz[10] have made an extensive and careful study of the relaxation of the MgO(001) surface, using twelve different interaction models, which include such effects as surface-induced changes in anion polarizability, quadrupole contributions to the total energy, and charge enhancement at the surface. It should be appropriate to compare the present results for MgO with those of Martin's and Bilz's model 2, which is a simplified version of the shell model of Sangster *et al.*[15] used in this work. It is found that, overall, the relaxation shifts are of comparable magnitude, but approximate agreement is found only for the Mg relaxation in the two outer layers. Again this lack of detailed agreement points to the delicate dependence of the results on the details of the relaxation models.

Comparison with the work of Welton-Cook and Prutton on alkali halides [Ref. 9(a)] and MgO [Ref. 9(b)] leads to similar conclusions. In general, the relaxation found by these authors for the alkali halides are between 2 and 10 times larger than found here (the only comparable case being NaF); the rumplings are comparable. For MgO the agreement is better than for the alkali halides; in particular, the rumple of -2.44% in the top layer agrees well with the low-energy electron-diffraction determination of -2% by Welton-Cook and Berndt.[16]

A final comparison can be made with the one-layer relaxation calculation of LiF by Cowley and Barker;[17] their cation and anion core shifts are about half of what we find for the top layer in our calculation. A reason for this small one-layer relaxation may be the circumstance, pointed out above, that a relaxing layer adjacent to the bulk acts as a transition layer, adjusting itself to the unrelaxed bulk. The difference in results between those of Ref. 17 and the present work has to be viewed in this light.

We conclude this discussion of the alkali halide results with the important observation that they provide an *a posteriori* justification for the validity of the dynamical calculations of Chen *et al.*[1] for the *unrelaxed* (001) surfaces of the alkali halides. The smallness of the relaxations make it plausible that the small error one makes in the equilibrium configuration, by placing the surface particles in their bulk rather than their relaxed positions, has a minimal effect on the calculated second derivatives of the total potential, i.e., on the vibrational frequencies of the system. Of course, other surface-related changes, such as changes in the anion static charges and polarizabilities, can occur, and can have an effect on the surface modes, but, in general, these effects are small. These facts have been borne out by the recent He scattering experiments of Brusdeylins *et al.*[3]

B. Lead sulfide

In the foregoing we discussed the surface relaxation of the alkali halides, which are weakly polarizable materials. However, the relaxation procedure can handle equally well strongly polarizable materials for which appropriate shell models are available. Interesting materials in this category are PbS and PbTe, which are narrow-gap semiconductors with the rocksalt structure. The difference in the calculated relaxation between these materials is the following: PbS is strongly polarizable, but its surface relaxation turns out to be convergent, like that of the alkali halides. PbTe, on the other hand, because of its large Te polarizability, exhibits a nonconvergent relaxation pattern involving the entire slab. Because of this qualitative difference, we have only included the results for PbS in Table II; the relaxation of PbTe will be discussed in a forthcoming paper. The results for PbS and PbTe can be summarized as follows:

(a) PbS (shell-model parameters given in Table IV). Most relaxation quantities (with the possible exception of z_c^+ in the center layer) are large compared to the same quantities for the alkali halides, and it takes more than ten layers to approach the bulk values (as opposed to fewer than four for the alkali halides). The relaxation is, however, convergent, and hence there is only a qualitative difference with the relaxation of the alkali halides but no quali-

TABLE IV. Shell-model data for PbS taken from M. Elcombe, Proc. R. Soc. London, Ser. A **300**, 210 (1967), model III, expressed in the same units as those of Table III.

A_{ss}^{+-}	B_{ss}^{+-}	$B_{ss\,\text{n-cent}}^{+-}$	A_{ss}^{++}	B_{ss}^{++}	A_{ss}^{--}	B_{ss}^{--}
42.0	-7.2	(-0.425)	-5.4	0.6	0.3	0.12
α_+	d_+	α_-	d_-	k_+	k_-	
5.125	-0.380	6.328	1.090	489.4	49.99	
X_+	Y_+	X_-	Y_-	Z	r_0	T (K)
-4.98	7.12	0.924	-3.064	2.14	2.968	300

tative difference.

(b) PbTe. The relaxation results, obtained with the shell model of Cochran *et al.*[18], show an unstable, nonconverging relaxation pattern. We believe that this represents an attempted reconstruction, which in the calculation is frustrated by the fact that the relaxing layers are sitting on top of a nonrelaxable bulk crystal. Since the frequency of the TO(Γ) mode of PbTe is temperature dependent and becomes almost soft at low temperatures, our results support the conjecture that a polarizability-related structural transition of PbTe (e.g., induced by lowering the temperature) might start at the surface and work its way into the bulk of the crystal. This could be an example of a much more general phenomena that any symmetry-lowering geometry in a crystal (surface, defect, interstitial, etc.) can be the center from which a structural transition starts growing into the crystal (in much the same fashion as nucleation centers are needed for solidification).

C. Final comment

Our calculations, both on the alkali halides and PbS and PbTe, show that the relaxed positions represent real minima of the potential with respect to the variations of the core and shell positions perpendicular to the (001) surface. However, we have to keep in mind the limitations of the present calculation: Calling reconstruction a surface rearrangement in which the two-dimensional surface unit cell is enlarged, we have not taken into account either the possibility of reconstruction or that of a relaxation of the cores and shells in the x-y plane. On the other hand, our calculations of the dynamics of the relaxed alkali halide and MgO slabs show that our relaxation procedure for these materials leads to true minima of the potential (phonon stability). In contrast, preliminary results of calculations of the dynamics of relaxed slabs of PbS and the other highly polarizable IV-VI compounds exhibit phonon instabilities, indicating that additional degrees of freedom are likely to play a role in the determination of the equilibrium positions of the cores and shells. When these additional degrees of freedom are taken into account, it may turn out that the relaxed positions for PbS, found in this work, are saddle points rather than absolute minima. These aspects will be discussed, together with the results for PbTe, in a forthcoming paper.

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APPENDIX A: COULOMB SUMS

The sums appearing in the expression for E_z^e [Eq. (9)] are summations over a 2D square lattice with lattice distance 1. In the *even* and *odd* cases, only terms for which l_1+l_2 is, respectively, even and odd, are taken in the summation (cf. Fig. 1). In a different approach, one can consider the even sum as a sum over a square lattice with lattice distance $\sqrt{2}r_0^2$ (solid circles in Fig. 1). In that case the expression for E_z^e is

$$E_z^e=-\frac{Q}{\sqrt{2}r_0}\frac{\partial}{\partial z}\left[\sum_{l_1,l_2}\frac{1}{[l_1^2+l_2^2+(z/\sqrt{2}r_0)^2]^{1/2}}-\frac{1}{\sqrt{2}r_0}\int\int\frac{ds_x ds_y}{(s_x^2+s_y^2+z^2)^{1/2}}\right]\Bigg|_{z=z_0}. \tag{A1}$$

Similarly, the odd sum can be considered as a sum over the same lattice, but taken with respect to the center of a square (open circles in Fig. 1). This leads to the expression

$$E_z^0=-\frac{Q}{\sqrt{2}r_0}\frac{\partial}{\partial z}\times\left[\sum_{l_1,l_2}\frac{1}{[(l_1-\frac{1}{2})^2+(l_2-\frac{1}{2})^2+(z/\sqrt{2}r_0)^2]^{1/2}}-\frac{1}{\sqrt{2}r_0}\int\int\frac{ds_x ds_y}{(s_x^2+s_y^2+z^2)^{1/2}}\right]\Bigg|_{z=z_0}. \tag{A2}$$

We now bring the expressions in (A1) and (A2) into rapidly converging form by the method of Nijboer and de Wette;[11] this will lead directly to the expressions given in (2a) and (3a).

We call the expressions inside the large parentheses in (A1) and (A2) $S^e(z)$ and $S^o(z)$, respectively. We write $S^e(z)$ and $S^o(z)$ in the form of an integral as follows:

$$S^{e,o}(z)=\int\int dx\,dy\frac{w^{e,o}(x,y)}{(z^2+y^2+\rho^2)^{1/2}}, \tag{A3}$$

where

$$w^e(x,y)=\left[\sum_{l_1,l_2}\delta(x-l_1)\delta(y-l_2)\right]-1, \tag{A4}$$

$$w^o(x,y)=\left[\sum_{l_1,l_2}\delta(x-l_1+\tfrac{1}{2})\delta(y-l_2+\tfrac{1}{2})\right]-1, \tag{A5}$$

and

$$\rho=z/(\sqrt{2}r_0).$$

We now make use of Parseval's theorem, which states that if $F(h_x,h_y)$ and $G(h_x,h_y)$ are the 2D Fourier transform of $f(x,y)$ and $g(x,y)$, then

$$\int\int dx\,dy\,fg^*=\int\int dh_x dh_y FG^*. \tag{A6}$$

According to this equality,

$$S^{e,o}(z)=\int\int dh_x dh_y FT_2[w^{e,o}(x,y)]FT_2[(x^2+y^2+\rho^2)^{1/2}]. \tag{A7}$$

One can show that[11]

$$FT_2[w^e(x,y)]=\left[\sum_{\mu_1,\mu_2}\delta(h_x-\mu_1)\delta(h_y-\mu_2)\right]-\delta(h_x)\delta(h_y)=\sum_{\mu_1,\mu_2}{}'\,\delta(h_x-\mu_1)\delta(h_y-\mu_2)\;, \tag{A8}$$

where $\sum_{\mu_1,\mu_2}$ is a summation over the reciprocal lattice of the original (l_1,l_2) square lattice, which is again a 2D square lattice, with lattice distance 1. The prime on the summation indicates that the term $\mu_1=\mu_2=0$ has to be excluded from the summation. In a similar fashion[11]

$$\begin{aligned}FT_2[w^o(x,y)]&=\left[\sum_{\mu_1,\mu_2}\delta(h_x-\mu_1)\delta(h_y-\mu_2)\exp[\pi i(h_x+h_y)]\right]-\delta(h_x)\delta(h_y)\\&=\sum_{\mu_1,\mu_2}{}'\,\delta(h_x-\mu_1)\delta(h_y-\mu_2)(-1)^{\mu_1+\mu_2}\;.\end{aligned} \tag{A9}$$

Finally,[11]

$$FT_2[(x^2+y^2+\rho^2)^{-1/2}]=(h_x^2+h_y^2)^{-1/2}\exp[-2\pi\,|\,\rho\,|\,(h_x^2+h_y^2)^{1/2}]\;. \tag{A10}$$

If we now substitute expressions (A8) and (A10) in $S^e(z)$ [Eq. (A7)], and (A9) and (A10) in $S^o(z)$, we have

$$S^{e,o}(z)=\sum_{\mu_1,\mu_2}{}'\,F^{e,o}(\mu_1,\mu_2)(\mu_1^2+\mu_2^2)^{-1/2}\exp[-2\pi\,|\,\rho\,|\,(\mu_1^2+\mu_2^2)^{1/2}]\;. \tag{A11}$$

Finally, substituting $S^e(z)$ into (A1) and $S^o(z)$ into (A2) leads directly to expressions (2a). The expressions (2b) for $E_z^{e,o}$ are obtained by applying the method of Nijboer and de Wette directly to Eq. (1). In that case we write

$$E_z^{e,o}=-\frac{Q}{r_0}\frac{\partial}{\partial z}\left[\sum_{\substack{l_1+l_2\\(\text{even, odd})}}\frac{1}{[l_1^2+l_2^2+(z/r_0)^2]^{1/2}}-\frac{1}{2r_0}\int\int\frac{ds_x ds_y}{(s_x^2+s_y^2+z^2)^{1/2}}\right]\Bigg|_{z=z_0}\;, \tag{A12}$$

where the sum is a double sum over l_1,l_2 such that l_1+l_2 is either even or odd. The derivation is completely analogous to the one above, but now we need the 2D Fourier transforms of the following sums of δ functions:

$$FT_2\left[\left[\sum_{\substack{l_1+l_2\\(\text{even, odd})}}\delta(x-l_1)\delta(y-l_2)\right]-\tfrac{1}{2}\right]=\tfrac{1}{4}\sum_{\lambda_1,\lambda_2}G^{e,o}(\lambda_1,\lambda_2)\delta(h_x-\tfrac{1}{2}\lambda_1)\delta(h_y-\tfrac{1}{2}\lambda_2)-\tfrac{1}{2}\delta(h_x)\delta(h_y)\;. \tag{A13}$$

The proof of this equality for the case l_1+l_2 even has been given by Chen;[19] the proof for the case l_1+l_2 odd is similar. Using these expressions together with (A10) in Parseval's expression and taking the limits $h_x,h_y\rightarrow 0$, occuring in both terms on the right-hand side of (A13), in the proper fashion, will, after a little algebra, lead to expression (2b) for $E_z^{e,o}$.

APPENDIX B: SHELL-MODEL PARAMETERS

In Table III we list the parameters of the shell models for the alkali halides and MgO, as they were taken from the literature. The short-range parameters in these models refer to shell-shell interactions. In addition, the models specify the electrical polarizabilities α and the mechanical polarizabilities d which are expressed in terms of shell charges Y and the core-shell force constants k,

$$\alpha_+=\frac{Y_+^2}{k_++R_0},\quad \alpha_-=\frac{Y_-^2}{k_-+R_0}\;, \tag{B1}$$

$$d_+=\frac{-R_0Y_+}{k_++R_0},\quad d_-=\frac{-R_0Y_-}{k_-+R_0}\;, \tag{B2}$$

where $R_0=A^{+-}+2B^{+-}$.

The model parameters given in the literature are given in the upper part of Table III. Usually, either B^{+-} or $B^{+-}_{\text{n-cent}}$ is given in the literature; in each case the derived quantity [cf. Eq. (12)] is given in parentheses. The quantities in the lowest six rows except for MgO are derived quantities; they follow from inversion of (B1) and (B2) and the relation $Z=X_++Y_+=X_-+Y_-$. For MgO the derived quantities in the entire column are given in parentheses.

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