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# A shell-model analysis of the structure and dynamics of crystal edges of alkali halides

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**Abstract.** The static relaxation and the lattice dynamics of rectangular edges of quadratic bars of four rock-salt-structured alkali halides is calculated using a shell model. The relaxation includes a large-scale contraction of the bar as well as tip-localized microscopic static displacements. The phonon spectra of relaxed quadratic bars are presented and modes localized at the edges are identified.

## 1. Introduction

During the last few decades the lattice dynamics of alkali halide surfaces has been thoroughly investigated and various surface modes have been found [1]. Such surface phonons have their maximum vibrational amplitude at the surface and are of plane-wave character parallel to the surface. One theoretical approach for the calculation of these modes is the so-called slab method. The aim of the present work is to find phonon modes at crystal edges which are localized at the tip of an edge and are extended along the edge. In a previous investigation [2] the slab method was extended to quadratic bars in order to study the statics and the dynamics of crystal edges. However, very simple rigid-ion models have been used, which only show qualitative trends, but do not give quantitatively reliable results. Based on these preliminary investigations an advanced approach to these systems is given using the shell model which, in addition to short-range and Coulomb interactions, also takes into account the polarizability of the ions [3, 4]. The shell model has proven to be a very reliable framework for the calculation of bulk and surface phonons of alkali halides [1]. Therefore edge-localized modes of alkali halides obtained by this approach are expected to be realistic.

Edges are of particular interest since symmetry is strongly reduced compared to that of the surface. This allows a more subtle investigation of the interatomic potentials. Moreover steps, i.e. edges, can be considered as one of the simplest types of defect of crystal surfaces which should be relevant in chemical processes (e.g. as catalysts).

The approach used here is valid for surfaces with high steps, in contrast to investigations dealing with small steps at surfaces [5]. Other investigations by Chen *et al* [6] were concerned with the lattice dynamics of finite microcrystals using a rigid-ion model. An advantage of the new approach lies in the one-dimensional translational symmetry, which allows for classification of the eigenmodes by their wave-vectors.

The paper is organized in the following way: in section 2 the application of the shell model for crystal bars is outlined, in section 3 the structure of the relaxed bar is discussed, and in section 4 the dynamics of quadratic bars is presented and edge-localized modes are identified. The results are summarized in section 5 along with conclusions.

## 2. Formalism

The shell model takes short- and long-range polarizabilities of the ions, Coulomb interactions and short-range interactions into account. In the same way as was done by Sangster *et al* [7] the short-range interaction is assumed to consist of two contributions: Born–Mayer potentials which exponentially decay and Van der Waals interactions as calculated by Ruffa [8] (see the appendix for details). The model parameters are obtained from a least-squares fit of the experimental data for the bulk crystals. Good agreement of calculated surface phonons with helium scattering data is achieved when using the following bulk properties as input data for the fit [9].

1. Dielectric properties, i.e. the static dielectric constant and the high-frequency dielectric constant.
2. Elastic constants:  $c_{11}$  and  $c_{12}$ .
3. Phonon frequencies at the  $\Gamma$ , X and L points obtained from neutron scattering.
4. The cohesive energy of the bulk.
5. The pressure derivative of  $c_{44}$ .

Experimental values for 1–4 are taken from [7], and for 5 are taken from [10]. For the calculation of surface and edge properties, the bulk potentials are used without modification.

The parameters used in this investigation fulfil the equilibrium condition of the bulk. Usually bulk shell models violate the equilibrium condition in order to simulate three-body interactions [11]. In the case of most alkali halides these interactions are small and may be neglected. Moreover breaking of the equilibrium condition would lead to a violation of the rotational invariance and thus to a non-vanishing frequency of the torsional acoustic mode of a relaxed bar in the long-wavelength limit [2, 6].

For the investigation of crystal edges a quadratic bar is used with (100) and (010) surfaces extending infinitely in the  $z$ -direction. The unit cell consists of the atoms of two neighbouring layers parallel to the  $x$ - $y$ -plane. The bar is constructed from the unit cell and a one-dimensional translation in the  $z$ -direction.

The relaxed atomic positions are determined by a Newton–Raphson scheme described in [12]. As in the case of alkali halide surfaces only few iterations are needed to achieve convergence.

The dynamics of the bar can be computed by a method similar to that of slab calculations [1]. Due to the periodicity of the lattice bar in the  $z$ -direction, the dynamical matrix can be written as

$$\mathbf{D}(q|\kappa\kappa') = \sum_l \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \phi \begin{pmatrix} 0 & l \\ \kappa & \kappa' \end{pmatrix} \exp[iq(z(0\kappa) - z(l\kappa'))]$$

with the one-dimensional wave-vector  $q$ , where  $l$  denotes the unit cell,  $\kappa$  is the atomic index inside the unit cell,  $\phi$  is the force constant matrix,  $m_\kappa$  is the mass of one atom and  $z(l\kappa)$  is the  $z$ -component of the position of an atom.

The Coulomb summation is done directly in real space by taking interactions with atoms within 40 nearest-neighbour distances ( $40r_0$ ) into account. For all of the calculations, quadratic bars with  $9 \times 9$  atoms per cross section (i.e. 162 atoms per unit cell) have been used if not stated otherwise.

## 3. Structure of the relaxed bar

At the surface of the unrelaxed bar the equilibrium condition is violated. This gives rise to relaxation normal to the surface as well as surface stresses.

**Table 1.** Distances between core positions of tip atoms and their second neighbours in the  $x$ - $y$ -plane in units of the bulk second-neighbour distance.

	NaCl	NaI	KBr	KI
Cation	0.96	0.95	0.97	0.96
Anion	0.97	0.98	0.97	0.98

This stress leads to a large-scale deformation of the bar, which leads to an inward motion of the tip atoms of about 5% of the nearest-neighbour distance away from its ideal position and falls off with increasing distance from the tip. Compared to the relaxation of the infinite surfaces of alkali halides the relaxation decreases very slowly and involves many atomic sites. The results are similar for NaCl and also similar to earlier findings for short-range interaction models [2]. This is not surprising, because the surface stress is primarily due to the lack of second neighbours at the surface [2, 6] and hence it is mainly governed by the short-range interactions.

Deformations caused by the surface stress are usually not observed in slab calculations due to the use of periodic boundary conditions. A similar contraction is found for KI and NaI. However, the pattern features additionally a strong inward relaxation of the surface cations.

For all four alkali halides the maximum contraction occurs at the tip of the bar. In table 1 the distance between a tip atom and its second neighbour in the  $x$ - $y$ -plane is given for the case of a  $9 \times 9$  bar. The distance is shortened by few per cent of the ideal distance and is quite independent of the size of the bar.

**Table 2.** Dipole moments of the edges and the surfaces of a relaxed  $9 \times 9$  bar in units of  $er_0$  as defined in the text.

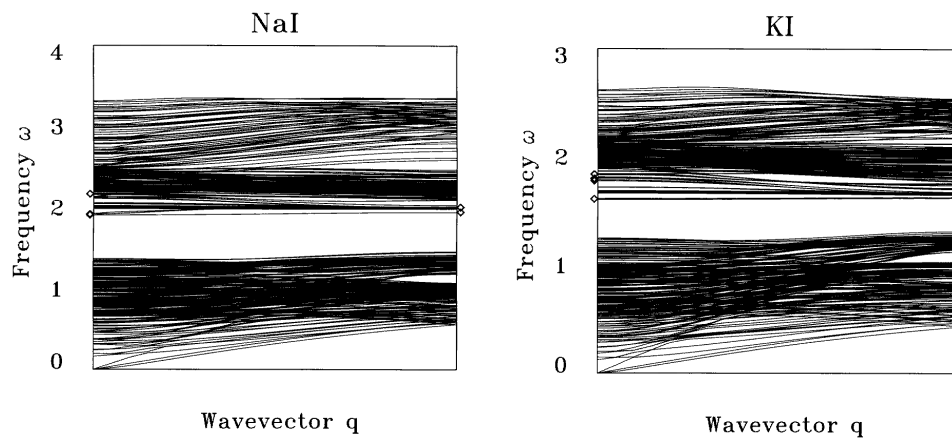
	NaCl	NaI	KBr	KI
<i>Cation</i>				
Tip	0.0258	0.0395	0.0278	0.0283
Next to tip	0.0160	0.0250	0.0177	0.0181
Middle of surface	0.0152	0.0238	0.0170	0.0174
<i>Anion</i>				
Tip	0.0399	0.0711	0.0402	0.0562
Next to tip	0.0240	0.0445	0.0243	0.0346
Middle of surface	0.0227	0.0405	0.0230	0.0324
<i>Total</i>				
Tip	0.0027	0.0038	0.0035	0.0035
Next to tip	0.0016	0.0024	0.0020	0.0021
Middle of surface	0.0015	0.0020	0.0018	0.0020

The main features of the microscopic displacements can be described in terms of dipole moments. The atomic dipole moment of a relaxed atom is defined by the product of shell charge times the distance between the core and shell of an ion [11]. The dipole moments of the tip atoms are almost twice as large as the dipole moments of the corresponding surface atoms. The relaxation of the atoms next to the tip atom is basically identical with the relaxation of atoms situated in the middle of one face (table 2). The atomic dipole of the cations is pointing inward, whereas the dipoles of the anions point away from the bar.

The absolute values of the  $x$ - $y$ -components of the total dipole moment calculated from the cores and shells of one pair of neighbouring atoms having identical ideal  $x$ - $y$ -positions are also given in table 2. The total dipole moment is also increased at the tip compared to the surface. However, due to the relative displacement of cations and anions it is strongly reduced compared to the atomic dipole moments. The total dipole moment of the tip is pointing inwards for all four alkali halides.

#### 4. Dynamics of relaxed bars

The phonon dispersion curves of crystal bars consist of three characteristic features: bulk bands, surface bands and edge modes which are fourfold degenerate in the chosen geometry. Since a quadratic bar has  $C_{4v}$  symmetry each edge-localized mode corresponds to one two-dimensional and two one-dimensional irreducible representations.

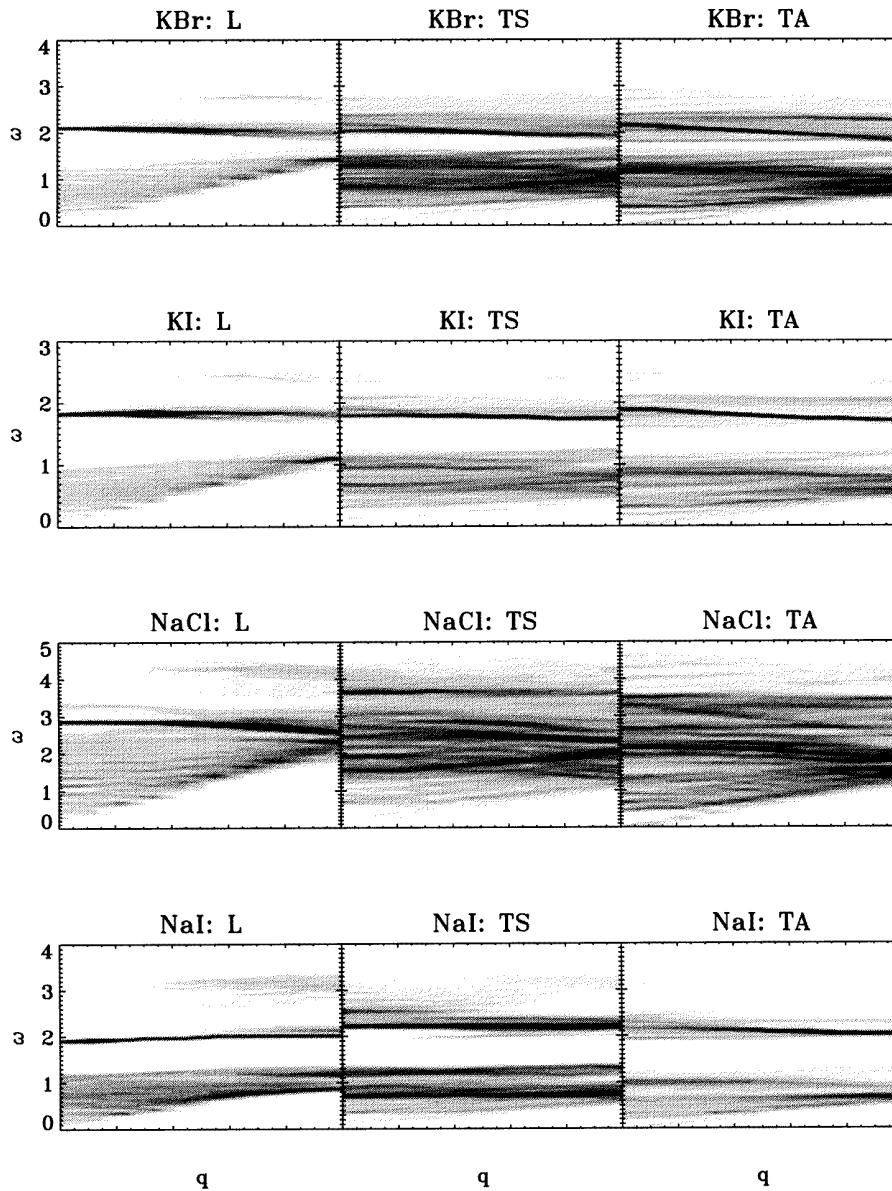


**Figure 1.** The phonon dispersion of the relaxed  $9 \times 9$  bars of NaI and KI. The wave-vector extends from  $q = 0$  to the zone boundary. The frequencies of edge-localized modes found by inspection of the eigenvectors are marked with  $\diamond$ .

As known from conventional calculations of surface dynamics, gaps can appear in the projected bulk dispersion where neither bulk nor surface states exist. Inside these gaps localized edge modes may be found. In figure 1 the dispersion relations of relaxed crystal bars of KI and NaI with  $9 \times 9$  atoms per cross section are shown. The corresponding dispersion relation for KBr looks similar; however, the gap is smaller; and for NaCl the projected density of bulk modes has almost no gap at all.

The macroscopic acoustic and optical modes have been discussed in detail in [2]. We will now discuss the microscopic modes using the more realistic shell model.

In KI and NaI some edge-localized modes can be identified easily since they are situated in the gap. In order to identify localized microscopic modes for NaCl and KBr, one can examine a modified problem by keeping two adjacent surfaces of a  $3 \times 3$  bar, and  $4 \times 4$  bar, respectively, fixed. Modes with a small amplitude near the fixed atoms are of particular interest. If the eigenvectors and eigenfrequencies of certain modes of the  $3 \times 3$  and  $4 \times 4$  systems are similar, one may conclude that these modes correspond to localized modes which might become resonant with surface- or bulk-type modes in larger bars. By comparison with the  $9 \times 9$  system, five edge-localized modes can be identified for  $q = 0$ :



**Figure 2.** The tip projected density of states  $\mathcal{J}(\omega, q)$  for longitudinal (L), transverse symmetric (TS) and transverse antisymmetric (TA) polarization for the four alkali halides KBr, KI, NaCl and NaI. Dark regions in the plot correspond to a high value of the projected density.

- $E_1$ : a longitudinal symmetric mode which is most strongly localized at the tip;
- $E_2$ : a transverse symmetric mode with main amplitudes at the tip;
- $E_3$ : a transverse antisymmetric mode with main amplitudes at the tip;
- $E_4$ : a transverse symmetric mode with main amplitudes at atoms next to the tip;
- $E_5$ : a transverse antisymmetric mode with main amplitudes at atoms next to the tip.

**Table 3.** Frequencies of edge-localized phonon modes of the alkali halides KBr, KI, NaCl and NaI within the shell model and of NaI within the short-range-interaction rigid-ion model (B) used in [2]. The first frequency corresponds to a  $4 \times 4$  bar with two adjacent surfaces kept fixed and the second to a  $9 \times 9$  bar with free surfaces. L (T) denotes modes with displacements mainly in the longitudinal (transverse) direction. S (A) denotes symmetric (antisymmetric) modes. A dash indicates that a mode could not be identified, brackets indicate a mode whose pattern is less clear due to hybridization. All frequencies are given in units of  $10^{13}$  rad s $^{-1}$ .

	KBr	KI	NaCl	NaI	NaI ([2], model (B))
<i>Zone centre</i>					
E <sub>1</sub> : LS	2.14	1.84	2.87	1.93	
	2.14	1.84	2.87	1.92	2.21
E <sub>2</sub> : TS	—	(1.91)	—	2.16	
	—	1.80	—	2.17	2.11
E <sub>3</sub> : TA	(2.16)	(1.89)	—	—	
	2.17	1.80	—	—	1.84
E <sub>4</sub> : TS	2.04	—	—	—	
	2.03	1.78	—	—	
E <sub>5</sub> : TA	(1.78)	1.60	—	1.90	
	1.81	1.61	—	1.91	1.94
<i>Zone boundary</i>					
E' <sub>1</sub> : LS	1.48	1.14	2.27	—	
	1.47	1.13	2.34	—	
E <sub>2</sub> : TS	—	1.76	—	2.13	
	—	—	—	—	1.95
E <sub>3</sub> : LTA	1.85	1.71	(2.65)	2.02	
	(1.82)	1.71	—	—	1.80
E <sub>4</sub> + E <sub>1</sub> : LTS	1.84	1.67	(3.70)	2.00	
	1.84	1.68	—	2.01	2.01
E <sub>5</sub> : LTA	1.85	1.62	—	1.94	
	1.87	1.63	—	1.95	1.92

For finite wave-vectors, transverse and longitudinal components mix. At the zone boundary, similar modes are found, which can be attributed to zone-centre modes as given in table 3. Furthermore a new mode appears at the zone boundary which is denoted by E'<sub>1</sub>.

In table 3 frequencies of tip-localized modes are listed for the four alkali halides. Also given in table 3 are the frequencies of localized modes found within the framework of a short-range-interaction rigid-ion model for NaI [2]. The eigenvectors and eigenfrequencies of localized modes compare well with the shell model for NaI.

In order to allow for comparison with experiments it is useful to calculate the projected density of states for different polarizations  $\xi$  given by

$$\mathcal{J}(\omega, q) d\omega = \sum_j \sum_{\substack{\omega_j \in [\omega, \omega + d\omega] \\ \kappa \text{ at tip}}} |\xi \cdot \mathbf{w}(\kappa, q|j)|^2$$

where  $j$  labels different phonon branches,  $\mathbf{w}$  is the normalized eigenvector, and  $\kappa$  is the index of atoms in the unit cell. Only atoms right at one tip are taken into account. Three polarizations  $\xi$  are considered: longitudinal (corresponding to the E<sub>1</sub> modes), transverse symmetric (E<sub>2</sub> modes) and transverse antisymmetric (E<sub>3</sub> modes). The densities are shown in figure 2. Regions with high projected densities correspond to localized modes as given in table 3. Moreover one can identify resonant modes easily, even if no edge modes can be found clearly by inspection of the eigenvectors (e.g. NaCl: TS).

## 5. Conclusion

This investigation presents a unified approach towards the statics and dynamics of crystal edges of alkali halides. The relaxation exhibits two characteristic features, a large-scale contraction of the bar and a tip-localized increase of the dipole moments. The total dipole moment of the edge is pointing inward. Due to the large-scale contraction it will not be sufficient in such systems to consider relaxation of a small number of surface layers only.

The dispersion relation reveals bulk bands, surface bands and localized edge modes. These edge modes have similar displacement patterns for the materials discussed. Moreover the modes found here are very similar to modes found using a simpler rigid-ion model and models using short-range interactions only [2].

A promising system for the experimental detection of edge modes would be a stepped surface with large steps. The (110) surface of NaCl is predicted to be unstable [13]. If this instability can be used for the generation of a regular array of edges, helium scattering experiments on this system would be of great interest.

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## Appendix. Potential parameters

The short-range potential acting between the shells of nearest-neighbour and next-nearest-neighbour atoms  $i$  and  $j$  is assumed to consist of Van der Waals interactions and Born–Mayer potentials:

$$V_{ij}^{\text{SR}}(r) = V_{ij}^{\text{vdW}}(r) + V_{ij}^{\text{BM}}(r) \quad (\text{A.1})$$

with the Born–Mayer potential given by

$$V_{ij}^{\text{BM}}(r) = a_{ij} \exp(-b_{ij}r) \quad (\text{A.2})$$

and the Van der Waals interaction by

$$V_{ij}^{\text{vdW}}(r) = \frac{c_{ij}}{r^6} + \frac{d_{ij}}{r^8}. \quad (\text{A.3})$$

Following Ruffa [8] the coefficients  $c_{ij}$  and  $d_{ij}$  are calculated solely from the shell charges  $Y_i$  and the harmonic core–shell coupling constants  $k_i$  (see [7] for details).

Using common notation, the longitudinal and transverse force constants of the short-range potential are written as

$$\frac{A_{ij}}{2} \frac{e^2}{2r_0^3} = \left. \frac{\partial^2 V_{ij}^{\text{SR}}}{\partial r^2} \right|_{r=r_{ij}} \quad (\text{A.4a})$$

and

$$\frac{B_{ij}}{2} \frac{e^2}{2r_0^3} = \left. \frac{1}{r} \frac{\partial V_{ij}^{\text{SR}}}{\partial r} \right|_{r=r_{ij}}. \quad (\text{A.4b})$$

Here  $r_0$  is the bulk equilibrium distance between nearest neighbours and  $r_{ij}$  is the bulk equilibrium distance between atoms  $i$  and  $j$ . In table A1 the parameters are listed.



**Table A1.** Potential parameters of the four alkali halides.  $X_i$  denotes the core charges,  $Y_i$  the shell charges ( $i = \pm$  for cations and anions respectively),  $k_i$  the shell-core coupling constant,  $r_0$  the nearest-neighbour distance, and  $A_{ij}$  and  $B_{ij}$  the longitudinal and transverse force constants.

	NaCl	NaI	KBr	KI
$X_+$ ( $e$ )	-2.327	-1.551	-3.294	-2.985
$Y_+$ ( $e$ )	3.320	2.556	4.280	3.972
$X_-$ ( $e$ )	2.016	2.568	2.001	2.941
$Y_-$ ( $e$ )	-3.008	-3.573	-2.987	-3.928
$k_+$ ( $e^2/2r_0^3$ )	367.8	171.7	620.1	528.4
$k_-$ ( $e^2/2r_0^3$ )	185.1	182.0	172.1	252.6
$r_0$ (Å)	2.789	3.194	3.262	3.489
$A_{++}$ ( $e^2/2r_0^3$ )	-0.042	-0.242	-0.210	-0.206
$A_{+-}$ ( $e^2/2r_0^3$ )	11.25	11.82	13.55	14.13
$A_{--}$ ( $e^2/2r_0^3$ )	0.031	0.382	-0.236	-0.088
$B_{++}$ ( $e^2/2r_0^3$ )	0.021	0.034	0.029	0.029
$B_{+-}$ ( $e^2/2r_0^3$ )	-1.289	-1.440	-1.35	-1.38
$B_{--}$ ( $e^2/2r_0^3$ )	0.050	0.098	0.079	0.093

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