

## Relaxation effects in the vibrations of a lithium fluoride surface

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The vibrational frequencies of a 15-layer slab are calculated for a simple shell model of lithium fluoride, and the surface modes occurring are analyzed. The static relaxations of a slab and of a single surface are calculated for the same model, and the effects of the relaxation on the vibrational frequencies are investigated. A puckering distortion of the surface layer is incorporated in the vibrational calculations for the first time and is found in this case to introduce one extra surface mode.

### I. INTRODUCTION

In recent years there has been growing interest in the surface vibrations of crystals. The surface vibrations of a crystal represent its means of coupling to the outside world and play a central role in determining such phenomena as energy exchange, trapping, adsorption, and desorption, and hence crystal growth. Most directly, the surface modes of vibration can be used to determine the scattering properties of the surface,<sup>1</sup> or, conversely, experimental observation of the scattering either of atomic beams or of synchrotron radiation can be used to infer the vibrational properties. Very recently, good-quality results on the alkali halides, sodium fluoride, and lithium fluoride, in particular, have been obtained using inelastic helium-atom scattering.<sup>2</sup>

There have been a number of calculations of the vibrational normal modes of ionic crystal slabs<sup>3-6</sup> or of the response functions associated with a single surface.<sup>7</sup> It has been established that the effects of polarizability of the ions, as described by the shell model, are significant. The importance of surface relaxation is less well understood. Static relaxation effects in a shell model have been studied,<sup>8,9</sup> and some of the effects of relaxation on the vibrations have been investigated for a rigid-ion model of a sodium chloride slab by Tong and Maradudin,<sup>3</sup> who did not include the possibility of puckering in the outer atomic layers. Chen and de Wette<sup>6</sup> have made some attempt to modify the parameters of a fitted shell model to allow for the surface relaxation, and most recently Benedik, Brivio, Miglio, and Velasco<sup>7</sup> have used empirically adjusted surface polarizabilities to reproduce observed features of the surface vibrations.

The main purpose of this paper is to show that relaxation effects can be included fairly completely in the calculation of surface vibrational frequencies, and that the relaxation can produce detailed changes in the structure of the surface-mode spectrum. A simple mechanical shell model of lithium fluoride was set up with fully defined potentials between the cores and shells (not just force constants), and surface relaxations, including puckering of the surface layer, were studied as a function of slab thickness. Calculations were then made of the vibrational frequencies of a fully relaxed 15-layer (001) slab. The only approximation made was that the surface distortion was restricted to the outermost layer. The effects of the relaxation are, in general, small, as was expected from the smallness of the relaxation itself, but a number of changes in the nor-

mal modes of the slab were discovered.

The model used and some features of the shell-model formalism, as applied to slabs, are described in Sec. II. The incorporation of the translation invariance conditions in the Coulomb sums has not previously been discussed in detail. In Sec. III, we describe the general features of the results and in Sec. IV, we discuss in detail the differences between results for unrelaxed and fully relaxed slabs for specific surface modes. Our result, which is not relevant to the discussion of surface modes but is important for the vibrations of a thin film is that the correct dispersion law for flexing modes of a plate<sup>10</sup> is obtained only for the fully relaxed slab.

### II. MODEL AND FORMALISM

Ideally the model used would provide an accurate description of the dispersion relations of the bulk solid and would also contain the exact volume and position dependence of the various parameters, such as force constants, so that the changes arising from relaxation can be incorporated. A shell model fitted to bulk dispersion relations satisfies the first requirement, but not the others. We have used such a model, derived by Dolling, Smith, Nicklow, Vijayaraghaven, and Wilkinson,<sup>11</sup> in a few calculations and obtained almost identical results to Chen *et al.*<sup>5</sup> However, it is difficult to incorporate relaxation effects in such a calculation. In particular, it is well known that the smaller force constants and some of the polarizability parameters in such a calculation are very sensitive to the details of the assumed model. It is, therefore, unreliable to fit an assumed form for an interatomic potential to the given force constants. We have, instead, used a simple shell model with forms for the interatomic potentials, assumed from the beginning, fitted to a small number of well-defined experimental quantities. Such a model does not reproduce exactly the bulk dispersion relations, but should be a reliable indicator of the changes which surface relaxation can produce.

We treat the lithium ion as a rigid point ion with charge  $e$ , where  $e$  is the magnitude of the electron charge. The fluorine ion consists of a shell with charge  $Ye$  and a core with charge  $-(1+Y)e$ , the two being joined by an isotropic spring of force constant  $k$ . There is a potential energy between the lithium ion and the fluorine shell, described by the expression

$$V_{12} = V_0 \exp(-r/\rho),$$

TABLE I. Values of the parameters.

Parameters of the model	
$V_0$	$5.58988 \times 10^{-10}$ ergs
$V_1$	$4.55865 \times 10^{-9}$ ergs
$\rho$	$0.28738 \times 10^{-8}$ cm
$C$	$2.17864 \times 10^{-58}$ ergs/cm <sup>6</sup>
$Y$	$-1.75264$
$k$	$6.8031 \times 10^5$ dyn/cm

and there is a potential between nearest fluorine shells described by

$$V_{22} = V_1 \exp(-r/\rho) - C/r^6.$$

The model thus contains six parameters, which were fitted to room-temperature values of the lattice spacing, two elastic constants,  $c_{11}$  and  $c_{44}$ , the two limiting optical vibrational frequencies, and the refractive index. The nearest-neighbor distance was taken to be 2.014 Å, and the values of the parameters are given in Table I. The use of room-temperature values for the experimental quantities is a crude way of absorbing some effects of anharmonicity.

The shell-model formalism, as applied to a slab, has recently been discussed by Chen *et al.*<sup>5</sup> and will not be described in detail here. Those authors describe the short-range part of the self-interaction elements arising from the condition of translational invariance, but they do not discuss corrections to the Coulomb part of the dynamical matrix arising from the same origin. When normal coordinates are introduced the Fourier-transformed equations of motion of the ion cores and shells can be written in matrix form as

$$\begin{aligned} \underline{m}\omega^2 \vec{U}_c &= \underline{A} \vec{U}_c + \underline{B} \vec{U}_s, \\ 0 &= \underline{B}^\dagger \vec{U}_c + \underline{D} \vec{U}_s, \end{aligned} \quad (1)$$

where  $\vec{U}_c$  and  $\vec{U}_s$  are the displacement amplitudes for cores and shells, respectively, and  $\underline{m}$  is a diagonal matrix of ionic masses. The Coulomb contributions to the matrices  $\underline{A}$ ,  $\underline{B}$ , and  $\underline{D}$  can be written explicitly as

$$\underline{A}(\text{Coulomb}) = \underline{X} \underline{C}_{cc} \underline{X} + \underline{A}_0,$$

$$\underline{B}(\text{Coulomb}) = \underline{X} \underline{C}_{cs} \underline{Y},$$

$$\underline{D}(\text{Coulomb}) = \underline{Y} \underline{C}_{ss} \underline{Y} + \underline{D}_0.$$

$\underline{X}$  and  $\underline{Y}$  are diagonal matrices of core and shell charges. The matrices  $\underline{C}_{cc}$ ,  $\underline{C}_{cs}$ , and  $\underline{C}_{ss}$  describe the Coulomb interactions between cores and cores, cores and shells, and

shells and shells, respectively, with no self-interaction terms included. Many authors have given explicit expressions for the matrix elements. We actually used a  $\Theta$ -function formula for the in-plane terms.<sup>12</sup> If all cores and shells are centered on the same sites  $\underline{C}_{cc}$ ,  $\underline{C}_{cs}$ , and  $\underline{C}_{ss}$  are identical. The two matrices  $\underline{A}_0$  and  $\underline{D}_0$  are chosen to satisfy the conditions that when all cores and shells are displaced uniformly, there should be no forces and no polarizing field acting on any ion. This leads to the results

$$\begin{aligned} (\underline{A}_0)_{k\alpha, k'\beta} &= -\delta_{kk'} X_k \sum_{k''} [C_{cc}(k, \alpha; k'', \beta; q=0) X_{k''} \\ &\quad + C_{cs}(k, \alpha; k'', \beta; q=0) Y_{k''}], \end{aligned} \quad (2)$$

$$\begin{aligned} (\underline{D}_0)_{k\alpha, k'\beta} &= -\delta_{kk'} Y_k \sum_{k''} [C_{cs}(k'', \beta; k, \alpha; q=0) X_{k''} \\ &\quad + C_{ss}(k, \alpha; k'', \beta; q=0) Y_{k''}]. \end{aligned}$$

Here  $k$  and  $k'$  number different sublattices.

It is usual to manipulate the equations of motion (1) by adding the second to the first and introducing a relative coordinate  $\vec{W} = \vec{U}_s - \vec{U}_c$ . The final form for the equations is then

$$\begin{aligned} \underline{m}\omega^2 \vec{U}_c &= (\underline{A} + \underline{B} + \underline{B}^\dagger + \underline{D}) \vec{U}_c + (\underline{B} + \underline{D}) \vec{W}, \\ \vec{0} &= (\underline{B}^\dagger + \underline{D}) \vec{U}_c + \underline{D} \vec{W}, \end{aligned}$$

and the matrices  $\underline{A}_0$  and  $\underline{D}_0$  are included at all appropriate places.

When the Coulomb matrices  $\underline{C}_{cs}$  and  $\underline{C}_{ss}$  are equal, the expression for  $\underline{D}_0$  reduces to

$$(\underline{D}_0)_{k\alpha, k'\beta} = -\delta_{kk'} Y_k \sum_{k''} C(k'', \beta; k, \alpha; q=0) Z_{k''}.$$

This form should be used, for example, in calculations involving an unrelaxed slab. It is interesting that it involves the ionic charges  $Z_k$ . The interpretation of this term is simple. If the electrostatic potential seen by an ion is expanded in a Taylor series about the ion site, there will, in general, be quadratic terms (which happen to vanish identically in the interior of diagonally cubic crystals). These terms modify the force constant linking the core and shell, and hence change the polarizability of the ion.

We believe that these corrections, which in the present application are very small, have not been included correctly in any previous slab calculations. Similar complications arise in calculations on bulk solids, when the ions do not sit at centers of symmetry, and have been discussed in that context by Cran and Sangster.<sup>13</sup>

As indicated above, we used a  $\Theta$ -function formalism to

TABLE II. Parameters of the relaxed structure as a function of slab thickness.

Number of layers	$r_0$ (Å)	$r_1$ (Å)	$u_1/r_1$	$u_2/r_1$	$w_2/r_1$
5	1.98704	2.03682	-0.00924	0.00377	-0.00522
10	1.99972	2.02591	-0.00957	0.00394	-0.00543
15	2.00430	2.02208	-0.00970	0.00399	-0.00552
25	2.00809	2.01892	-0.00981	0.00402	-0.00560
100	2.01252	2.01528	-0.00994	0.00406	-0.00570
200	2.01328	2.01466	-0.00996	0.00407	-0.00572
$\infty$	2.01404	2.01404	-0.00998	0.00407	-0.00573

TABLE III. Surface reconstruction and surface energy  $\sigma$  for three models of LiF.

Model	$u_1/r_0$	$u_2/r_0$	$w_2/r_0$	$\sigma$ (erg/cm <sup>2</sup> )
Rigid ion	-0.001 05	-0.004 42		745.89
Point dipole	-0.055 21	-0.011 07	-0.038 58	648.47
Shell	-0.009 98	0.004 07	-0.005 73	731.25

transform the Coulomb sums into a rapidly convergent form. However, for the changes in the sums when the surface plane puckers, this proved inconvenient, and we used a simple real-space summation for the changes. This is inelegant, but gave adequate accuracy for a rather small effect, which has not previously been considered at all.

### III. RESULTS

#### A. Static relaxation

The static energies of both a finite thickness slab and a single surface were minimized with respect to the positions of the atoms in the surface layer. For the single surface, the outward displacements  $u_1$ ,  $u_2$ , and  $w_2$  of the lithium ion, fluorine core, and fluorine shell were determined by a numerical iterative procedure. In the case of the finite thickness slab, the nearest-neighbor distances parallel to the slab,  $r_0$ , and perpendicular to the slab,  $r_1$ , were also allowed to vary. These, in fact, are the most important relaxation effects. The details of the electrostatic sums required are almost all available in the literature.<sup>3,14</sup> The short-range contributions to the energy were evaluated using a literal interpretation of a mechanical shell model, e.g., the distance from the lithium ion to the fluorine shell appears in the nearest-neighbor potential. The results of the energy minimization for slabs of varying thickness are given in Table II. The infinitely thick case corresponds to a single surface. The displacements of the outermost lithium ion, fluorine core, and fluorine shell relative to the second layer are  $u_1$ ,  $u_2$ , and  $w_2$ , respective-

ly;  $u_1$  and  $w_2$  are negative (inward relaxation).

As a matter of interest, the calculations for the single surface were repeated with two slightly changed models. In the point-dipole model, the parameters were unchanged, but the short-range interatomic forces were assumed to act on the fluorine core, rather than on its shell. In the rigid-ion model, the fluorine core and shell were constrained to move together. The results for the three models are shown in Table III, together with the surface energies. The results are similar to those found by other authors<sup>8,14</sup> in that the rigid-ion model gives very small relaxations and a correspondingly small correction to the surface energy, while the point-dipole model greatly overestimates both.

#### B. Normal modes of vibration

The vibrational frequencies of a slab are best discussed in terms of the corresponding bulk normal modes. If the faces of the slab are perpendicular to the  $z$  direction, the  $x$  and  $y$  components of the wave vector are still good, and the dispersion relations resemble those of the bulk crystal projected onto this two-dimensional wave vector.<sup>4</sup> The hatched areas in Figs. 1 and 2 show such projections for the present model for the  $\Sigma$ , [100] direction and the  $\Delta$ , [110] direction, respectively. In both cases, the normal modes can be classified<sup>4</sup> as sagittal plane (SP) modes, having eigenvectors lying in the sagittal plane which contains  $z$  and  $\bar{q}$ , or as shear horizontal (SH) modes with eigenvectors perpendicular to this. Most of the calculated frequencies for the slab lie in the hatched regions, but a few modes are split off from the bulk continuum. These are the surface modes which are of interest in the present cal-

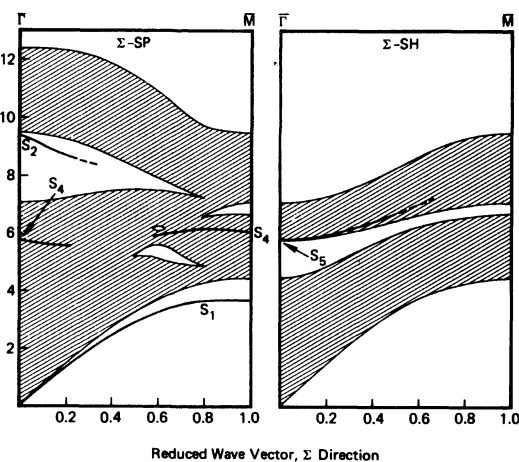


FIG. 1. Bulk phonon dispersion relations for the simple shell model projected onto the  $\Sigma$ ,  $[\xi, 0, 0]$  direction. The modes are divided into SP vibrations with polarization vectors  $(x, 0, z)$  in the sagittal plane, and SH vibrations with polarization vectors  $(0, y, 0)$ . Also shown are characteristic surface modes found for the fully relaxed slab.

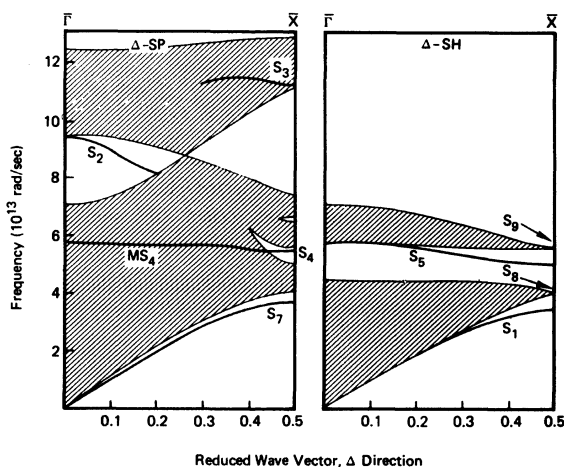


FIG. 2. Bulk phonon dispersion relations for the simple shell model projected onto the  $\Delta$ ,  $[\xi, \xi, 0]$  direction. The SP modes have polarization vectors  $(x, x, z)$  and the SH modes have polarization vectors  $(x, -x, 0)$ .

TABLE IV. Selected frequencies in units of  $10^{13}$  rad/sec at the  $\Gamma$ ,  $X$ , and  $M$  points in the surface Brillouin zone: (a) unrelaxed shell model fitted to bulk phonon frequencies, (b) unrelaxed simple shell model, (c) simple shell model with relaxed lattice spacings, and (d) simple shell model with relaxed lattice spacings and reconstructed surface layer.

	(a)	(b)	(c)	(d)	
$\Gamma$	$\omega_{\max}$	12.384	12.347	12.263	12.264
	$S_2$		9.345	9.309	9.352
	$S_{4,5}$	5.319	5.539	5.781	5.787
$X$	$\omega_{\max}$	11.555	12.771	12.831	12.832
	$S_3$	10.285	11.031	11.160	11.162
	$S_9$		5.636	5.776	5.822
	$S_4$	5.486	5.391	5.389	5.432
	$S_5$	4.744	4.804	4.984	4.990
					4.114
	$S_7$	3.671	3.700	3.691	3.686
$S_1$	2.988	3.283	3.375	3.418	
$M$	$\omega_{\max}$	8.567	9.438	9.577	9.579
	$S_4$	5.829	5.914	5.790	6.040
	$S_1$	3.793	3.722	3.676	3.697

ulation. Various surface modes at  $\Gamma(\vec{q}=0)$  and at the two zone boundaries are indicated by the arrows and labels. We have followed as far as possible the notation of Chen, de Wette, and Allredge<sup>5,6</sup> in labeling the surface modes. Thus  $S_1$  is the lowest branch in each direction. In the  $\Sigma$  direction, this is the SP Rayleigh wave, but for most of the  $\Delta$  direction it is an SH vibration. Benedek *et al.*<sup>7</sup> have used the label  $S_1$  exclusively for the Rayleigh wave. At  $\vec{q}=0$ ,  $S_4$  and  $S_5$  are the transverse-optic surface modes identified by Lucas.<sup>15</sup>  $S_5$  remains a true surface mode over much of the zone.  $S_4$  lies in the continuum of SP modes and is not a true surface mode. Chen *et al.* label it  $MS_4$ . We have indicated this branch in the regions where it could easily be identified.

We have made calculations of the frequencies for four models: an 11-parameter shell model fitted to bulk phonon dispersion relations with no allowance for relaxation,<sup>11</sup> the present potential model with the ions occupying undistorted bulk positions, the present model with values of  $r_0$  and  $r_1$  corresponding to the relaxed slab, and the fully relaxed model in which the parameters  $u_1$ ,  $u_2$ , and  $w_2$  are introduced. A comparison of the results indicates which variations are model dependent and which arise from the surface relaxation. The frequencies of the labeled surface modes are given for these four models in Table IV, together with the maximum frequencies at the three wave vectors, to indicate the variations of the bulk bands between the different models.

#### IV. DISCUSSION

The model we have used is sufficiently simple and physically well defined that we have been able to carry out a consistent calculation of the effects of surface relaxation on both the static and vibrational properties. However, because of this simplicity, the model does not reproduce exactly the properties of the bulk solid. Columns (a) and (b) of Table IV show some frequencies for an unrelaxed

slab calculated with a model fitted to the bulk solid and with the present model. There are differences of up to 10% in some of the surface mode frequencies between the two models, and, in addition, column (b) shows two extra surface modes for the simple model. The results of column (a) are almost identical with those of Chen *et al.*<sup>5</sup> for the same model, most of the difference arising from our use of the mean atomic mass for Li. The  $S_2$  mode at  $\Gamma$  was found by Chen *et al.* for a number of alkali halides.

The remaining columns show the effects of relaxation on the surface mode frequencies and should be compared with column (b). The results in column (d) show the effect of puckering in the surface layer of atoms. The fluorine ions relax outward relative to the lithium ions and also acquire a dipole moment even in their equilibrium positions. This effect has not previously been included in any calculations. It has the effect for our model of introducing one extra surface mode at the point  $X$ . This mode, which we have labeled  $S_8$ , and an additional mode  $S_9$  do not seem to correspond to any of the labels given by Chen *et al.*<sup>5</sup> Both are shear horizontal modes in which the maximum vibration amplitude occurs in the second atomic layer.  $S_8$  is split off from the transverse-acoustic bulk band and is predominantly a vibration of the fluorine ions.  $S_9$  is split off from the transverse-optic band and is predominantly a vibration of the lithium ions.

Experimental results have recently become available, mainly for the  $S_1$  branch along the  $\Sigma$  direction.<sup>2</sup> An interesting feature of the results is that, near the zone boundary, the branch is flatter than the calculations suggest, so that at the  $M$  point the calculated frequency is too high. The measured value is about  $3.4 \times 10^{13}$  rad/sec. All calculations to date give values higher by 5–12%. Benedek *et al.*<sup>7</sup> have shown that if the fluorine-ion polarizability is increased by 17%, the measured frequency is obtained, and they suggest using different values for the polarizability in the interior of the crystal and at the surface. We

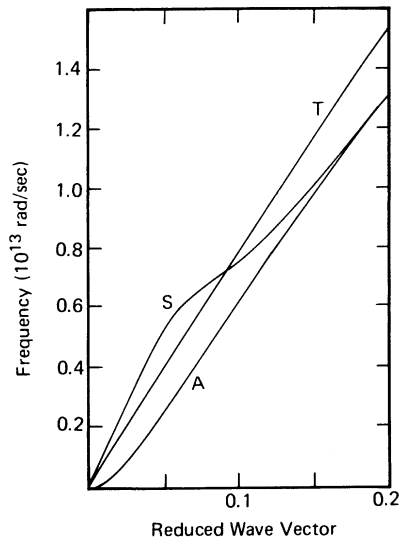


FIG. 3. Lowest three branches of the dispersion relation for small wave vectors in the  $\Sigma$  direction for the fully relaxed model.  $T$  is a transverse mode with polarization vector  $(0, y, 0)$ .  $S$  and  $A$  are polarized in the sagittal plane and are, respectively, symmetric and antisymmetric with respect to the center of the slab.

would like to point out that the shell model already incorporates this effect, since the removal of neighboring layers of atoms removes some contributions from the dynamical matrix, one result being a change in the polarizability perpendicular to the surface. In our model, the polarizability is increased by almost 9%. Similarly, the shell model does attempt to describe changes in the Szigeti effective charge at the surface. Relaxation of the surface layer does reduce the  $S_1$  frequency at  $M$  somewhat, and if the decrease which we calculate due to relaxation were incorporated into the more sophisticated breathing shell model of Benedek *et al.*,<sup>7</sup> about half the discrepancy with the experiment would be removed.

Of the remaining changes which occur when the surface layer is relaxed and reconstructed, one of the largest is that the Lucas modes,  $S_4$  and  $S_5$  at  $\vec{q}=0$ , increase in frequency and move back to the edge of the transverse-optic band. A consequence of this is that the  $S_5$  branch is less well separated from the continuum. It may make unambiguous identification of these modes more difficult experimentally.

We have also examined the behavior of the lowest-frequency surface acoustic modes at long wavelengths. Figure 3 shows the results for the  $\Sigma$  direction. Over most of the zone, there is a doubly degenerate branch  $S_1$ , which is the Rayleigh surface wave. As the wavelength increases, the penetration depth of the wave also increases, and for a finite thickness slab, it ceases to be a surface wave. The two branches now split. The symmetric branch moves into the bulk continuum band and takes on the character of a longitudinal-acoustic mode. The antisymmetric branch becomes a flexing mode of the plate with the unusual property that the frequency varies as the square of the wave vector. The branch marked  $T$  in Fig. 3

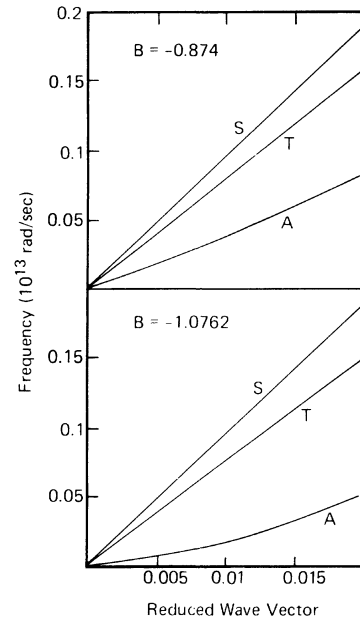


FIG. 4. As Fig. 3, but for the unrelaxed shell model fitted to bulk frequencies. The upper results are for fitted value of the parameter  $B$ , and the lower results have  $B$  adjusted, as described in the text.

is a conventional transverse-acoustic branch, polarized in the plane of the slab. This behavior was discussed on the basis of macroscopic elasticity theory by Lamb.<sup>10</sup> The upper part of Fig. 4 shows similar results for the unrelaxed model, fitted to bulk dispersion relations. Note that only very small wave vectors are shown. The quadratic region in the antisymmetric branching is missing. We interpret this as indicating that the model represents a plate under stress. In fact, if the parameters of the model are interpreted in terms of two-body forces in the usual way, even the bulk solid is under stress. In the bottom part of Fig. 4, we have adjusted the value of a single parameter  $B$  to satisfy the bulk equilibrium condition. The behavior of the antisymmetric branch is seen to be much more nearly quadratic.

This illustrates the main source of difficulty in this work. While the models used in calculations of bulk dispersion relations can reproduce the experimental results closely, the physical interpretation of the parameters is not straightforward, and the fitted lattice-dynamical model can contain, implicitly, unwanted stress effects. Use of such a model to predict relaxation phenomena is then unreliable. The model we have used is a very simple one. Only one ion is polarizable, the ionic charge is fixed at  $e$ , and breathing effects are neglected. Probably by eliminating some of these restrictions, we could get better agreement with experiment. However, because the model is so basic, it is probably a good indicator of the importance of effects such as relaxation in both static and vibrational properties. This is a difficult problem, and we believe that our approach gives valuable insight into it.

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