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Rapid Communications

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New surface mode on the (001) surfaces of RbBr and RbI

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We describe the appearance of a new, relaxation-induced, transverse-optical surface mode *above* the bulk continuum in RbBr and RbI. Because of its polarization perpendicular to the surface, the mode should be amenable to experimental verification by inelastic He scattering. The discussion includes other perpendicular surface modes such as the "optical" and the "acoustical" Rayleigh modes.

In recent years inelastic He scattering[1] and electron-energy-loss spectroscopy (EELS)[2] have developed into important experimental techniques for the study of surface dynamics of crystals. The first measurements of complete surface-mode dispersion curves were carried out with He scattering for the (001) surface of the alkali halides.[3] More recently, both He scattering and EELS studies have concentrated mainly on the dynamics of metal and semiconductor surfaces.

In this Rapid Communication we draw attention again to the alkali halide surfaces because our present theoretical work indicates that possibly there are a number of interesting surface dynamical phenomena still to be observed, expecially in the heavier alkali halides.

One can argue that at the present time surface dynamical phenomena are the most completely understood (next to the noble-gas solids) for the alkali halides, because for these compounds the dynamical description can be based on bulk shell models (SM's) which have a firm microscopic foundation. The parameters of these models can be obtained from bulk phonon dispersion curves. As a consequence, this has been the one area in surface dynamics in which theoretical predictions have preceded experimental confirmations by a number of years.[4,5]

The first He-scattering experiments were almost exclusively restricted to measurement of the low-lying acoustic surface modes, particularly the acoustic Rayleigh mode. More recently, higher-lying surface modes have also been detected. The optical surface modes are especially of great interest, because these modes are particularly sensitive to details of the interaction models and to the surface relaxation. Thus, measurement of these modes can contribute significantly to a more complete understanding of static and dynamic surface phenomena.

We recall that the measurements of the Rayleigh mode on the (001) surfaces of NaF, NaCl, and KCl agreed very well with theoretical predictions for *unrelaxed* surfaces[3] (LiF being the exception). This seemed to indicate that effects of surface relaxation on the surface dynamics of these crystals are small. To investigate this question in detail we have carried out a survey of the dynamics of the relaxed (001) surfaces of the alkali halides[6,7] and have found that, indeed, for the lighter alkali halides which were studied experimentally, the effects of relaxation on the surface dynamics are minimal. However, this is not true for the heavier alkali halides; in particular in RbBr and RbI there are new relaxation effects, not encountered in any of the other compounds.

The relaxation and dynamical calculations of the alkali halides can both be based on bulk SM's available in the literature. Because of the closed-shell configurations, the short-range repulsive interactions are adequately described by Born-Mayer potentials which can be derived from the bulk SM parameters. The polarizabilities of the models describe the most important effects of electrical and mechanical electronic deformation, and the Coulomb interactions can be treated exactly. Thus, all the forces on the ionic cores and shells can be evaluated as functions of position. In this way we can carry out an iterative surface relaxation calculation, in which we require that in the final relaxed configuration the net forces on cores and shells have vanished. For alkali halides this turns out to be a rapidly converging procedure, and the resulting surface relaxation is found to be limited to at most the four outer layers of the crystal.[6] In general, the atomic force constants in the relaxed positions will be different from their bulk values, so that we can expect effects of relaxation on the dynamics.

In our relaxation calculations we find that RbBr and especially RbI, as a result of their large overall polarizabilities, show the largest surface relaxations of all alkali halides. In RbI the core and shell shifts in the top layer are of the order of 6% of the lattice constant. These relaxed configurations were used as the equilibrium configurations in dynamical calculations on 15-layer slabs with (001) surfaces.

In Figs. 1 and 2 we display the slab dispersion curves for RbBr and RbI, for wave vectors along the boundary $\bar{\Gamma}\bar{X}\bar{M}$ of the irreducible surface Brillouin zone, in the top panel for the unrelaxed slab, and in the bottom panel for the relaxed slab. The solid curves represent surface-localized modes, the dashed curves the so-called bulk bands. Two things are immediately obvious: first, that the surface mode spectra are rather complex and second, that in each case there are significant differences between the unrelaxed and the relaxed cases.

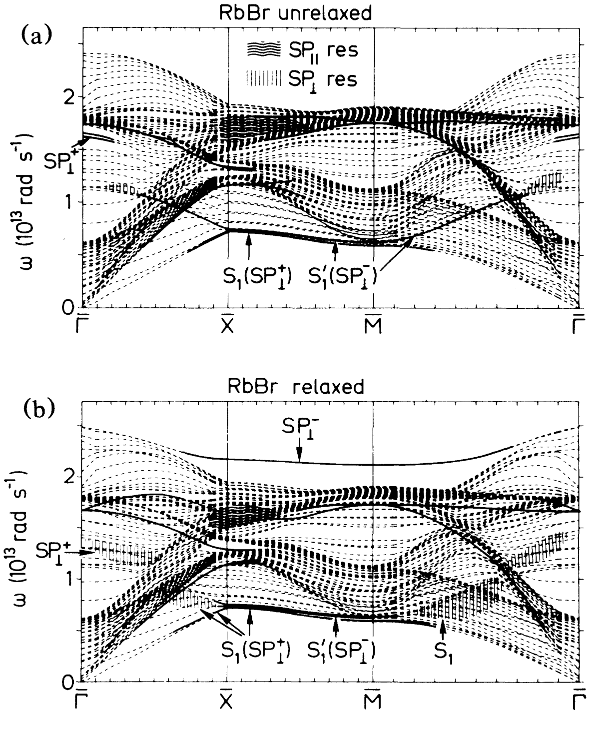

FIG. 1. Phonon dispersion curves for 15-layer unrelaxed and relaxed slabs of RbBr with free (001) surfaces. S_1 and S_1' indicate the acoustical and optical Rayleigh modes, respectively. SP$_\parallel$ and SP$_\perp$ indicate longitudinal and transverse sagittal-plane vibrations. The hatched areas indicate resonances of the type indicated. Only surface modes with vibrations perpendicular to the surface have been identified.

This is not the place to describe in detail the variety of surface modes encountered in these cases; for a general characterization of surface modes in alkali halides we refer to Chen, de Wette, and Alldredge.[4] However, we point out that for the unrelaxed surfaces, for wave vectors in the directions $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{M}$, because of symmetry, the dynamical matrix factorizes into two separate representations, one containing two-thirds of the modes with particle vibrations in the sagittal plane (SP) (the plane of the wave vector and the surface normal), the SP modes, and the other containing one third of the modes with particle vibrations perpendicular to the sagittal plane (i.e., parallel to the surface), the shear horizontal (SH) modes. If an SP vibration is polarized predominantly (or completely) parallel to the surface it is longitudinal and indicated by SP$_\parallel$; if it is polarized predominantly (or completely) perpendicular to the surface it is indicated by SP$_\perp$. The SP$_\perp$ modes are of particular importance for He scattering, because these are the modes that interact most strongly with the He atoms and therefore, in general, have the largest inelastic scattering cross sections.

The most pronounced relaxation-induced feature in both RbBr and RbI is the isolated surface mode above the bulk continuum. This is a surface mode which is raised out of the transverse optical bulk band due to increased forces resulting from the inward relaxation of the surface layer of the crystal. Vibrations in this mode are localized in the two outer layers of the crystal: In the top layer the lighter

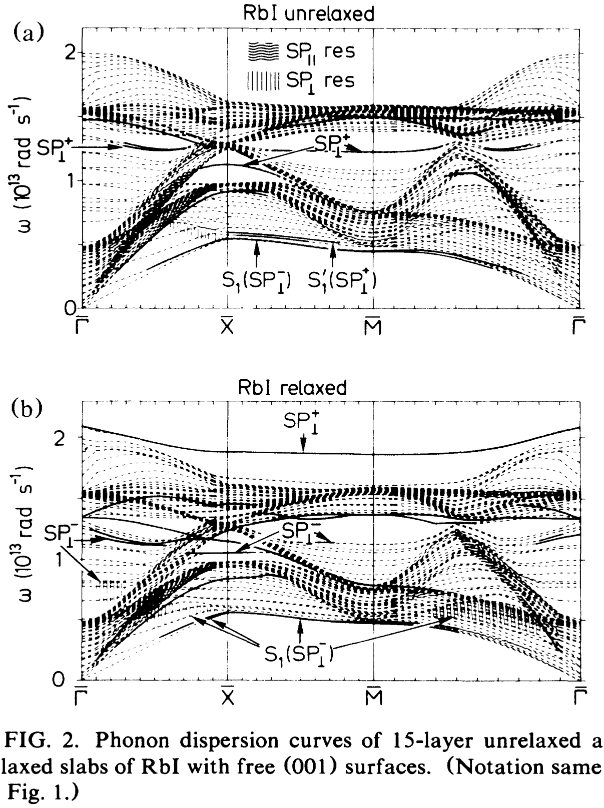

FIG. 2. Phonon dispersion curves of 15-layer unrelaxed and relaxed slabs of RbI with free (001) surfaces. (Notation same as in Fig. 1.)

of the two ions vibrates perpendicular to the surface ($SP_\perp$), while the heavier ion is at rest; in the second layer the heavier ion vibrates (also $SP_\perp$) with an even larger amplitude, while the light ion remains at rest. (The frequencies of this mode for the high-symmetry points $\bar{\Gamma}$, $\bar{X}$, and $\bar{M}$ are given in Table I.)

We believe that this new mode, if it exists, should be more easily detectable in RbBr than in RbI for the following reasons: In RbBr it is the Br ion that vibrates in the top layer, and the fact that it is the larger of the two ions facilitates the interaction with the He atoms. On the other hand, in RbI it is the Rb ion that vibrates in the top layer; since its ionic radius is quite a bit smaller than that of the I ion it is much less exposed to the incoming He atoms. Furthermore, there is the additional circumstance that the contribution of this mode to the mean-square amplitude of the vibrating top-layer atom is quite small: For instance, at room temperature, it is roughly 1% of the neighbor distance (versus 4% for the Rayleigh mode). This should be more of a drawback for detection of the mode in RbI than in RbBr for the reasons given above. Finally, we expect that, because of the high mode energy and the small amplitude, this mode will be much more difficult to detect than the Rayleigh mode.

Returning to Fig. 1(b) we point out that in addition to the acoustical Rayleigh mode S_1, on the interval $\overline{XM}$, there exists just above S_1 an "optical" (or second) Rayleigh mode S_1', first discussed for NaF, NaCl, and KCl by de Wette, Kress, and Schröder.[8] It has the same transverse-optical vibration pattern as the new mode discussed above, namely, in the top layer the lighter of the two ions vibrates perpendicular to the surface and the heavier ion is at rest. (In the acoustical Rayleigh mode this is the other way around.) In an experiment S_1' can, of course, not be distinguished from S_1, so we expect that in RbBr the effect of S_1' will be an apparent enhancement of the Rayleigh mode at both $\bar{X}$ and $\bar{M}$. In RbI [Fig. 2(b)] the mode only occurs in the neighborhood of $\bar{M}$, so the enhancement should only occur at $\bar{M}$.

Finally, in Fig. 1(b), we point out a very broad $SP_\perp$ resonance on both intervals $\overline{\Gamma X}$ and $\overline{\Gamma M}$. In this resonance the predominant motion is by the heavy particle (Rb^+), so that it has the character of an acoustical vibration. In this sense it might be considered as an example of a "folded prolongation" of the Rayleigh mode, as discussed by Benedek and Miglio.[9] In the unrelaxed case the resonance is much narrower and has both acoustical and optical vibrational character.

In relaxed RbI there exists on the interval $\overline{\Gamma X}$ a fairly well defined surface mode with perpendicular vibration ($SP_\perp^-$) between 1.1×10^{13} and 1.2×10^{13} rad sec^{-1} which reappears in the longitudinal-transverse-acoustical bulk band gap around $\bar{X}$. This mode might also be a good candidate for experimental verification. In unrelaxed RbI a similar mode exists, but here its vibrational character is $SP_\perp^+$; it is a prominent feature in the optical-acoustical gap along the zone boundary and around $\bar{M}$.

TABLE I. Frequencies of new surface modes in RbBr and RbI (in 10^{13} rad sec^{-1}) at high-symmetry points of the surface Brillouin zone.

	RbBr	RbI
$\bar{\Gamma}$	· · ·	2.087
$\bar{X}$	2.168	1.877
$\bar{M}$	2.133	1.862

The purpose of this Communication is to point out the appearance of a new, relaxation-induced surface mode in RbBr and RbI, based on relaxation and surface dynamical calculations carried out with published bulk shell models. Since the vibration in this mode is normal to the surface, it is a good candidate for experimental verification.

If this mode is indeed found to exist this would confirm, first, that surface relaxation has an important effect on the dynamics in RbBr and RbI (since the mode is not present for the unrelaxed surfaces) and, second, that the bulk SM's used in the calculation can indeed be relied upon to lead to reliable predictions for surface dynamics.[10] Furthermore, the existence of the mode would be an implicit confirmation of the correctness of our relaxation procedure, namely, use of Born-Mayer potentials for the short-range interactions, change in force constants in accordance with these potentials, and the use of relaxed structures as obtained in Ref. 6.

If, on the other hand, the mode is *not* found, this would indicate that the bulk SM's are not fully appropriate for surface dynamics. The SM's would then have to be refitted to make them consistent with both bulk and surface dynamical results. This would be an example of the more stringent requirements which the presence of a surface imposes on ionic interaction models. Moreover, other interpretations based on these bulk SM's, such as the interpretation of Raman spectra, would then have to be reexamined.

In addition to the new mode with frequencies above the bulk continuum, described here for the first time for alkali halides, we have also discussed other modes with similar vibrational patterns. A more complete discussion of all the surface modes appearing in Figs. 1 and 2 will be published elsewhere.

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[10] For RbBr and RbI this is still somewhat of an open question because, although these SM's correspond to overall "best fits" to bulk dispersion curves, some of the parameters in these models have rather unphysical values.