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Interpretation of features in the surface-phonon dispersion curves of KBr(001) and RbBr(001)

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The crossing surface mode and an anomaly in the optical surface-phonon dispersion recently observed in KBr(001) by means of helium scattering are analyzed and interpreted on the basis of a Green's-function calculation of KBr(001) surface dynamics. The nature and origin of crossing modes in isobaric crystals like RbBr and nonisobaric crystals like KBr are reexamined in light of a general mechanism based on LA-LO hybridization in the ⟨100⟩ direction. Their dispersion is then accounted for in terms of zone-boundary bands, specifically TA_2. LA-LO hybridization is also invoked to explain the anomaly observed in the optical surface mode.

The first high-resolution He-atom–surface scattering experiments were carried out on the (001) surface of LiF.[1] Since then a number of similar experiments have been carried out on other alkali halides, KCl,[1] NaF,[1-3] NaCl,[4] RbCl,[5] RbBr,[6] KBr,[7] and NaI,[8] a sufficient number for the general features of surface-phonon dispersion common to all these materials to be discerned. In all of these crystals the Rayleigh wave has been observed and generally found to have the largest intensity among the He-atom–one-phonon scattering events. In many of these compounds longitudinal-acoustic modes and optical modes have also been observed across the surface Billouin zone. The character of these modes was easily assigned by associating them to the lower edges of the four bulk phonon bands polarized in the scattering (sagittal) plane.

In NaF (along $\bar{\Gamma}\bar{X}$) (Ref. 9) and KCl (along $\bar{\Gamma}\bar{M}$) (Ref. 1) additional modes, termed as crossing modes, were observed. These modes appear as optical modes in that they have nonzero frequency at $\bar{\Gamma}$, and become very close in energy to the Rayleigh wave at $\bar{X}$ or $\bar{M}$. Unlike the ordinary surface branches which run along the bulk band edges, these modes cross the acoustic band with negative group velocity. An explanation to account for the existence of such crossing resonant modes was offered by Benedek and Miglio.[10] The argument is an extension of the one formulated for the bulk by Foldy, Witten, and Segall,[11,12] who suggested that isobaric crystals (i.e., with nearly equal masses of alkali and halide ions) should have a vibrational pattern similar to the corresponding monatomic crystal with half the lattice spacing. Thus the associated monatomic lattice has a simple cubic Brillouin zone which encloses the true fcc Brillouin zone [Fig. 1(a)]. Then, the optical modes of the isobaric alkali halide should arise as a folding back of the acoustic modes in the extended Brillouin zone into the fcc zone. This leads to a folding plane which contains the hexagonal face of the fcc zone and the high-symmetry points *L*, *K*, *U*, and *W*. Inspection of bulk dispersion relations of NaF, KCl, and RbBr [Fig. 1(c)] (Ref. 13) indeed shows an approximate degeneracy of acoustic-optical mode pairs at the points on the hexagonal face. Segall and Foldy point out that neutron scattering experiments confirm this to be the case for the isobaric alkali halide bulk phonons.

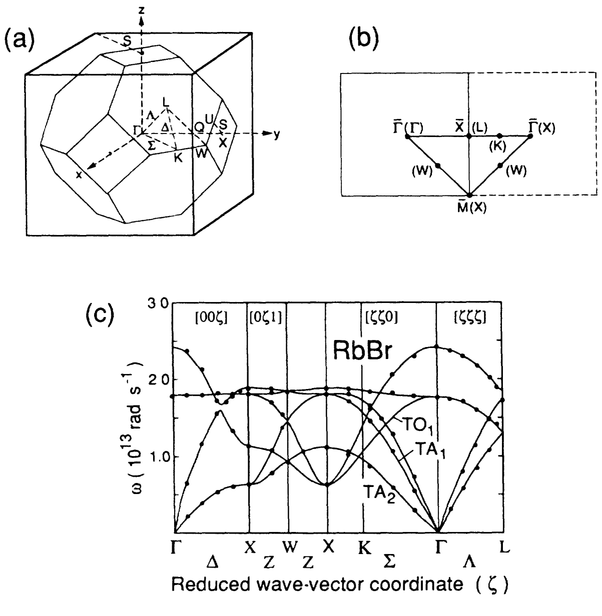

FIG. 1. (a) Brillouin zone for fcc crystals, adapted from Ref. 12. (b) Surface Brillouin zone for fcc (001) surface; letters in parentheses give the corresponding points in the bulk zone which project onto the surface zone. (c) Bulk dispersion curves for the isobaric crystal RbBr taken from Ref. 13; approximate acousto-optical degeneracy occurs at the points *L*, *K*, and *W* which are located on the folding plane containing the hexagonal face of the Brillouin zone.

This point of view has been adapted to the two-dimensional Brillouin zone by Benedek and co-workers,[9] who noted that the $\overline{XM}$ edge of the surface Brillouin zone for the isobaric diatomic fcc crystal is a folding line for the surface branches of the corresponding monatomic simple cubic lattice [Fig. 1(b)]. According to this scheme, the folded branch in the $\overline{\Gamma X}$ direction is just the continuation of the Rayleigh branch along the same direction in the extended zone, whereas the folded branch in the $\overline{\Gamma M}$ direction comes from the contour segment $\overline{XM}$ of the extended zone. Green's-function (GF) calculations for NaF and KCl (Ref. 10) confirm the existence of folded modes, in agreement with the above argument and with experiment. For RbBr no GF calculation is available, but slab calculations by de Wette *et al.*[14] show clear evidence for the crossing resonance and the folding of the Rayleigh branch along the zone contour $\overline{XM}$. Our experimental results for RbBr,[6] shown in Fig. 2 together with the dispersion curves of de Wette and co-workers, confirm the existence of a folded mode in both directions. However, the first theoretical evidence for a crossing resonance, obtained long ago by the Green's-function method,[15] was in NaCl, which is not isobaric. Although the mass misfit in NaCl (as in RbI) is not dramatic ($[M_+/M_-]^{1/2}=0.81$), Benedek *et al.*[9] found that another mechanism for the crossing modes may work regardless of the isobaric condition, particularly at the zone center.

These authors noted that the folded branch in NaF(001) is restricted to large wave vectors and yields no new surface resonance around the zone center. Its natural continuation, if anticrossing with the upper mode is disregarded, would be the ordinary Lucas mode (S_4). In contrast, in KCl and NaCl the crossing mode exists as a new, independent resonance, extending up to the zone center, where it takes the character of the so-called structure-induced surface resonance discussed by Stroscio *et al.* for metal surfaces.[16] This mode descends from the LA bulk mode at the $X(001)$ point due to the fact that at such a point the LA dispersion curve exhibits a relative minimum. Such a minimum, produced by the LA-LO hybridization along the ⟨100⟩ direction, occurs in KCl and NaCl, but not in NaF. It was also noted that the structure-induced resonance at the zone center must be purely shear vertical because it is generated by a bulk longitudinal band. Table I lists the alkali halide crystals with rocksalt structure where the minimum induced by such hybridization is either strong (in this case we report the corresponding frequency) or weak or does not appear at all. We note that in general, large gaps reduce the hybridization between acoustic and optical modes and therefore large differences in mass work against structure-induced resonances. However, the opposite is not true, as shown by the NaF case.

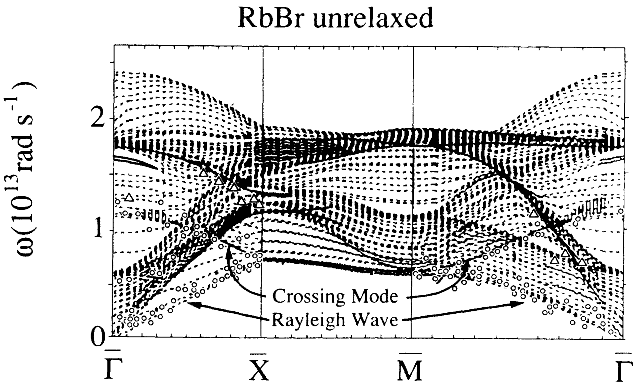

FIG. 2. Experimental (Ref. 6) and theoretical (Ref. 14) surface-phonon dispersion curves for RbBr(001); the crossing modes are evident in both high-symmetry directions.

TABLE I. The alkali halides with rocksalt structure where the LA-LO hybridization along the ⟨100⟩ direction yields a relative minimum in the LA dispersion curve at X. When the minimum is pronounced and may cause the appearance of a structure-induced resonance, the corresponding frequency is given (in 10^{13} rad/sec).

	F	Cl	Br	I
Li	None	None	None	None
Na	None	2.72	Weak	1.20
K	None	2.04	1.38	0.99
Rb	Weak	Weak	1.11	0.84
Cs	Weak			

Another, rather different explanation was suggested by de Wette *et al.*[17] who found evidence for crossing modes in slab dynamics calculations for alkali halides which are clearly not isobaric, such as KBr. They argue, instead, that these modes arise because of the hybridization (i.e., polarization exchange) between the bulk TA_1 and TO_1 in the ⟨110⟩ direction [Fig. 1(c)], and have sagittal polarization. According to this mechanism, one should be able to predict the existence of the crossing mode from the bulk dispersion curves by checking whether, near the midpoint of the ⟨110⟩ direction in the three-dimensional Brillouin zone, the two modes do show avoided crossings, namely an exchange of vibrational character. On this basis de Wette *et al.* predict sagittal resonances for NaF, NaCl, KCl, KBr, RbBr, and RbI. In their slab calculations they find clear evidence for this crossing mode in the first four of these compounds, doubtful evidence for RbBr, and no evidence for RbI.[14]

In our laboratory at Florida State University (FSU) we have carried out high-resolution He-scattering experiments on RbBr (Ref. 6) (Fig. 2), KBr (Ref. 7) (Fig. 3), NaI,[8] NaCl,[18] and RbCl.[5] The results for KBr(001), reproduced in Fig. 3, are compared with the GF calculation of the dispersion curves by Benedek and Miglio.[10] For RbBr and KBr we find crossing modes in both high-symmetry directions. In NaI a crossing mode is found in both directions only at long wavelengths; for NaCl we have some evidence for a crossing mode along $\overline{\Gamma M}$. In on-going experiments in this laboratory there is also some evidence for a crossing mode in RbI along $\overline{\Gamma M}$. The respective experimental frequencies at the zone center are listed in Table II, together with a previous datum for KCl,[1,19] and are compared with the X-point LA frequencies reported from Table I. No evidence for a crossing mode was found in RbCl (Ref. 5) and LiF,[1] in agreement with Table I.

Such a good correspondence supports the general idea that the crossing mode, as such, is a structure-induced mode. It is not necessarily a true resonance in the sense that a pole might not be found in the perturbed Green's function. (This seems to be the case for KBr and NaI, at least within the resolution affordable in a numerical Green's-function calculation performed in the early nineteen seventies.) The surface-projected van Hove singularity associated with the LA minimum may be enough to yield observable peaks in the surface-phonon density. This is clearly seen in the calculated surface-projected phonon densities of KBr(001) for sagittal polarization, extracted from the old Green's-function calculation[10] and shown in Figs. 4(a) (⟨100⟩ direction) and 4(b) (⟨110⟩ direction). The main features of the calculated spectra (denoted by S_1, Rayleigh wave; S_2, shear vertical optical mode; S_4, sagittal Lucas mode; S_6, quasi-longitudinal-acoustic mode; S_8, crossing mode) correspond quite well to the experimental peaks (black dots; the arrows indicate the position of the TA_2 mode, whose dispersion, as explained below, determines that of the crossing mode). The S_8 feature appears to be sharp and strong enough to be easily observed in scattering experiments although no pole of the perturbed Green's function can be associated with it.

We want to stress, however, that the folding mechanism operating in NaF, KCl, and RbBr generates real surface modes, so that a structure-induced mode continuing as a folded branch (as in KCl and RbBr) is itself a surface resonance. Conversely, a folded branch need not end up in a structure-induced mode; when such a mode is not allowed, as in NaF, the folded branch is connected to an ordinary optical surface mode.

TABLE II. Experimental crossing mode frequencies at the zone center (in units of 10^{13} rad/sec) compared to the bulk LA frequency of the relative minimum at X.

Crystal	Experimental	LA frequencies at X
NaCl	2.5[a]	2.72
NaI	1.25	1.20
KCl	2.0[b]	2.04
KBr	1.35	1.38
RbBr	1.15	1.11
RbI	0.86[c]	0.84

[a] Estimated value because only a few data points exist in this region; uncertainty is about 0.2.

[b] A few more data, besides those of Ref. 1, have been collected in the $\overline{\Gamma M}$ direction and reported in Ref. 19, which permit us to calculate this value.

[c] Preliminary experiments in this laboratory.

With regard to the peculiar, downward dispersion of the crossing mode from the zone center towards the zone boundary in the high-symmetry directions, a further comment is in order. We note that the bulk LA(X) frequency is the same as that of the extension of the TA_2 mode in the ⟨110⟩ direction at (1,1,0), which is the X point of the next zone. The polarization of this mode is

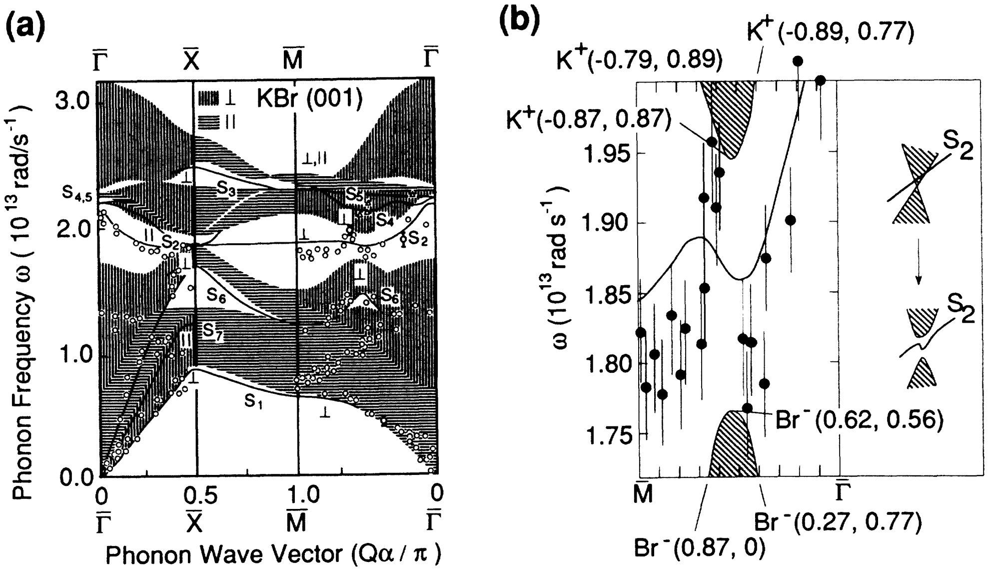

FIG. 3. Experimental (Ref. 7) and theoretical (Ref. 10) surface-phonon dispersion curves for KBr(001). In (a) the crossing modes are evident in both high-symmetry directions. (b) The experimental points and the theoretical optical surface mode in the gap are shown with a magnified frequency scale to display the anomalous bump; a representation of the hybridization mechanism producing the anomaly is shown schematically in the inset.

(0,0,1)—that is, transverse—and on the surface it should project as a sagittal mode. Thus we suggest that the dispersion of the crossing mode along the $\overline{\Gamma X}$ direction originates from that of the TA_2 mode, which in the bulk has the proper polarization to project onto the surface as a sagittal mode. Moreover, in three dimensions this mode extends over the whole region from point Γ to X [i.e., (0,0,0) to (1,1,0)], while the surface Brillouin zone $\overline{\Gamma X}$ is exactly half of this distance [from (0,0,0) to $(\frac{1}{2},\frac{1}{2},0)$]. Thus it appears that the crossing mode in the two-dimensional zone arises from the folded portion of this mode which in three dimensions extends into the next zone. It is noteworthy that for most of the alkali halides the TA_2 mode is the lowest transverse-acoustic mode in the region from Γ to K, the major exception being LiF, for which the TA_1 mode with polarization $(-1,1,0)$ lies lowest.

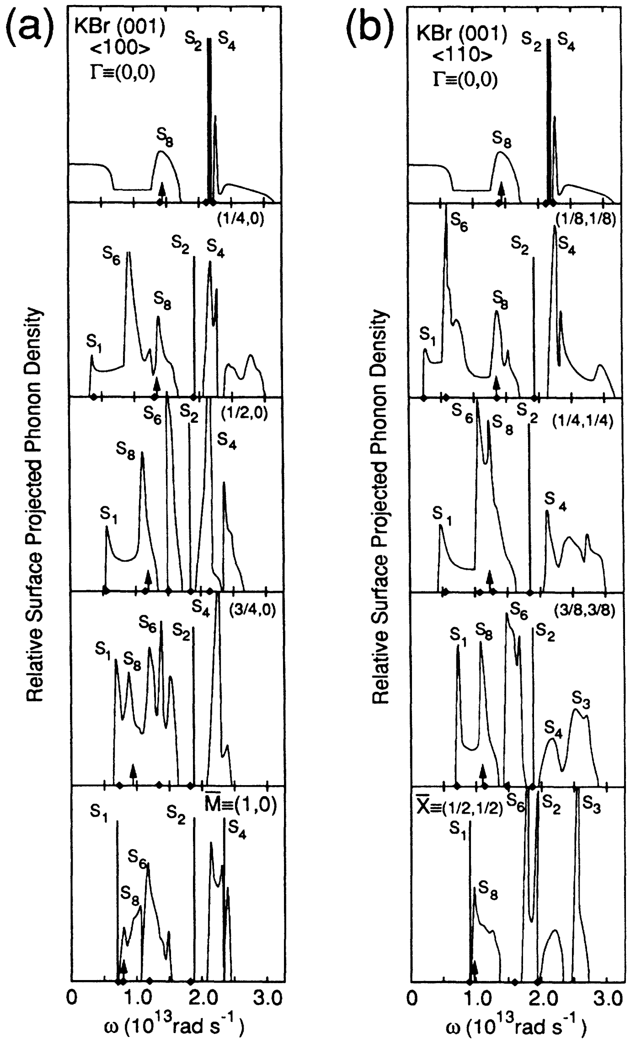

FIG. 4. Surface-projected phonon densities of KBr(001) for sagittal polarization, calculated with the Green's-function method, (a) for points in the $\overline{\Gamma M}$ direction and (b) for points in the $\overline{\Gamma X}$ direction. Solid points on the abscissa are the data of Fig. 3(a). The arrows show the position where the bulk TA_2 dispersion data would lie (from Ref. 13), in close correspondence with the observed crossing mode.

For the other symmetry direction, $\overline{\Gamma M} = \langle 100 \rangle$, it is not quite as straightforward (Fig. 1). The first half of this region, from (0,0,0) to $(\frac{1}{2},0,0)$, should contain the projection of the bulk mode from (0,0,1) to $(\frac{1}{2},0,1)$ with polarization (0,0,1). This is equivalent by symmetry to the transverse bulk mode going along XW and polarized perpendicular to the square face of the fcc Brillouin zone. Again, this mode is sagitally polarized at the LA(X) frequency. For the second half of this region, from $(\frac{1}{2},0,0)$ to (1,0,0) (i.e., to $\overline{M}$, which is the projection of another X point), the mode which appears to be relevant is the other transverse mode in the square face of the next zone. This plane begins at W but is perpendicular to the first. Hence, this mode is equivalent to the in-plane transverse mode which goes from W to X. At W the two transverse modes have the same frequency and at X the in-plane mode has the frequency of the TA mode at X. The combination of the two gives the crossing mode in $\overline{\Gamma M}$. From the symmetry, and more along the analogy with the folding picture, the sagittal projection of the above modes from point X to W to X can be seen to lie along $\overline{\Gamma M}$ in the second surface Brillouin zone [Fig. 1(b)]. Hence one could ascribe this crossing mode as arising from the folding back of this sagittal projection into the first Brillouin zone.

The detailed Green's-function calculation available for KBr permits us to discuss here another interesting experimental feature of its surface dispersion curves, which also appears to originate from LA-LO hybridization. The experimental points for the gap mode S_2 agree quite well with the calculated curve in both symmetry directions [Fig. 3(a)]. Also a small detail, the bump occurring in the middle of the $\overline{\Gamma M}$ direction is qualitatively reproduced, but the experiment shows a much larger oscillation. This is better seen on the enlarged frequency scale in Fig. 3(b). Here the solid line is the detailed S_2 dispersion curve, calculated by the Green's-function method, on a finer mesh. The shaded areas represent the upper and lower edges of the LA and LO bulk bands, respectively, in their anticrossing region. The inset shows pictorially that there is no special physics in the anomalous bump; it is just a hybridization effect of the surface mode with two bulk edge modes. Assuming that in the absence of certain interactions all of the three modes would cross each other (upper inset), one would expect the hybridization to result in anticrossing and to give the observed configuration (lower inset).

The much larger oscillation observed in the experimental data may then be interpreted in the following way. Figure 3(b) gives the x and z displacement components of the K^+ ions in the sagittal plane for the LO mode (Br^- ions are almost at rest) and of the Br^- ions for the LA mode (K^+ ions are almost at rest) at three different positions of their respective dispersion curves. At the LA edge, the polarization goes from x to mainly z in moving from left to right of the maximum. At the optical edge, the polarization is slightly more z on the left and slightly more x on the right of the minimum. Thus, due to hybridization, the band edges show a partial exchange of character. He-atom scattering intensity is proportional to the square of the displacement, and is normally much larger for z displacements than for x displacements. Moreover, the scattering from larger ions like Br^- is normally more intense than from smaller ions like K^+. Hence, if some additional scattering from the z-polarized edges occurred in the region where the gap mode gets close to the band edges, an apparent shift of the scattering peak towards the z-polarized edges would be observed with a consequent magnification of the bump. Of course, better resolution would enable one to distinguish the intensity due to the surface gap mode from that due to bulk edge minima and maxima.

We conclude that the appearance of peaks in the inelastic spectra termed as crossing modes in KBr, as well as in the other alkali halides listed in Table I, is the result of the projection of the bulk modes existing for the most part at the boundary of the three-dimensional Brillouin zone. Under special conditions (e.g., equal masses) a genuine surface resonance may be generated below the edge of the folded TA_2 band. This, however, does not appear to be a necessary condition for a crossing mode to be observed. In this work we present evidence that such an observation is rather general and in agreement with the calculated surface-phonon densities.

A detailed Green's-function calculation of the gap mode dispersion relation in KBr(001) also accounts qualitatively for the anomalous experimental bump, and suggests LA-LO hybridization as a possible mechanism for the anomaly and for the amplification of the effect observed in the experiment.

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