Evidence for the shear horizontal phonon mode on the NaCl(001) surface

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High-resolution He atom inelastic-scattering experiments provide evidence for the shear horizontal surface phonons on the *in situ* cleaved NaCl(001) surface. The measurements were made in a sagittal plane along the [210] azimuth and beyond the first surface Brillouin zone. A slab calculation using the breathing shell model and a surface perturbation that fulfills invariance conditions is used to identify the polarizations of the observed surface phonons. [S0163-1829(96)09247-8]

I. INTRODUCTION

Helium atom scattering (HAS) and electron energy loss spectroscopy (EELS) have provided nearly all presently available information on the dispersion curves of the fundamental microscopic vibrational processes occurring at surfaces.[1–4] However, much of the previous scattering work with either HAS or EELS was carried out for surface phonons propagating along high symmetry directions where symmetry conditions limit the excited surface phonons to those modes with sagittal polarization. These studies provide a wide spectrum of surface vibrations including those with vibrations transverse to the surface (called Rayleigh waves RW or S_1) and the quasilongitudinal acoustic modes and resonances as well as higher-energy optical modes with polarizations in the sagittal plane.[2] Along high symmetry directions for surfaces with complete reflection symmetry,[5] however, there are also modes (sometimes called S_7 modes) with exact *shear horizontal* (SH) polarization,[5,6] i.e. polarization in the surface plane and perpendicular to the phonon wave vector $\boldsymbol{Q}$. If the scattering plane is a sagittal plane and also a plane of reflection symmetry the SH modes cannot couple to the probing He atoms for symmetry reasons.[7]

Surface SH modes have been previously detected by EELS on a few metal surfaces with hexagonal symmetry[8,9,7] and on graphite.[10,11] However, no evidence for SH modes on insulator surfaces has been reported. Early attempts to find SH modes using HAS were based on tilting the scattering plane away from the normal but did not provide any evidence for SH modes.[12,13] However a hybridization of the S_1 with the shear horisontal S_7 mode did appear to manifest itself along the surface Brillouin zone edge between $\bar{\Gamma}$ and $\bar{M}$ as was observed on the surface of LiF(001).[13]

Measurements of the SH modes are important because (i) they provide a further condition on surface interionic potentials, (ii) they make possible the determination of the microscopic shear forces of surface stress in materials, and (iii) in studies of one material epitaxially grown on another, the SH mode may change significantly and thus provide information on the microscopic shear forces at the interface between the two different materials. Furthermore, the SH modes are more sensitive to shear interfacial forces than the Rayleigh or longitudinal modes.

Previously there have been a number of HAS studies on NaCl(001),[14,15] and recently several new features have been observed.[16,17] In this work, we report experimental results on the acoustic SH mode on the NaCl(001) surface, which are interpreted by comparison with a theoretical analysis of the data.

II. EXPERIMENT

The HAS spectrometer used in these experiments has been described in detail elsewhere[18] and is an upgraded version of the first Göttingen apparatus.[19] A nearly monoenergetic ($\Delta E/E \leqslant 2\%$) thermal energy He beam is produced by a continuous expansion of helium gas; the beam then passes through a skimmer followed by a chopper for time-of-flight (TOF) measurements. After several stages of differential pumping the helium collides with the crystal surface. Following the scattering, the helium atoms pass into a detector chamber where the beam flux is measured by a magnetic mass spectrometer operated in a single ion counting mode. The base pressures are in the low 10^{-11} mbar in both the detector and target chambers. In this apparatus the sum of the incident (Θ_i) and the final (Θ_f) scattering angles of He atoms is fixed ($\Theta_i + \Theta_f = 90°$). Different surface wave vectors are accessed by rotating the crystal around an axis normal to the scattering plane.

From each TOF spectrum, the energies of the phonons $\hbar\omega$ can be easily identified and from the conservation equations the associated parallel wave-vector transfers $\mathbf{\Delta K}$ can be calculated. To analyze the data it is convenient to refer to the *scan curve*, which relates all possible wave-vector transfers $\mathbf{\Delta K}$ and energy transfers $\hbar\omega$ with the incident angle Θ_i and the initial parallel wave-vector component $K_i = k_i \sin\Theta_i$:[22]

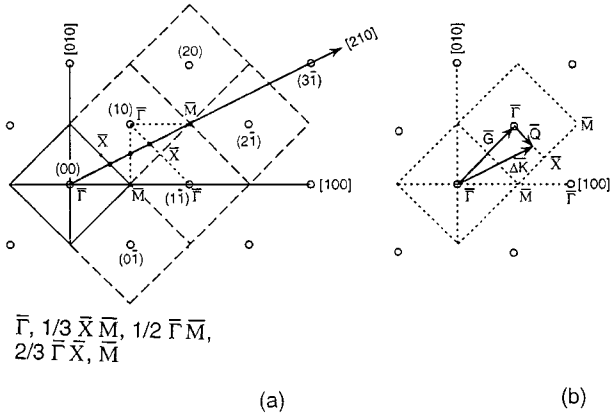

FIG. 1. Reciprocal lattice geometry for the NaCl(001) surface (a) showing the high symmetry directions as well as the [210] direction and (b) the parallel wave-vector components for phonon modes at $\boldsymbol{Q}=2/3\bar{\Gamma}\bar{X}$. $\boldsymbol{G}$ is the reciprocal lattice vector, $\boldsymbol{Q}$ is the phonon wave vector, and $\Delta\boldsymbol{K}$ is the parallel momentum transfer in the scattering plane.

$$\hbar\omega = -E_i + E_i(1+\Delta K/K_i)^2 \frac{\sin^2\Theta_i}{\sin^2\Theta_f}. \tag{1}$$

The NaCl crystal[21] target used in this work had dimensions $6\times10\times10$ mm^3 with about 3×3 mm^2 exposed to the beam. It was cleaved *in situ* at scattering chamber pressures in the mid 10^{-11} torr range. The incident He beam energy was variable in energy, however, 20 meV provided an optimal energy resolution in the phonon energy range studied. The temperature of the crystal was fixed at $T_s=100$ K during the measurements. This temperature is low enough to keep the multiphonon background small, yet high enough to provide for a significant single-phonon signal and avoid adsorption of the residual gases in the scattering chamber.

III. RESULTS AND DISCUSSION

In order to observe SH modes, one has to remove the mirror symmetry of the sagittal plane in the high symmetry directions. This can be achieved by either tipping the scattering plane away from the surface normal[13] or by exploring regions of parallel momentum transfer **ΔK** outside the first Brillouin zone along an azimuthal direction away from a high symmetry direction. Thus umklapp phonons originating from reciprocal lattice vectors $\boldsymbol{G}$ out of the scattering plane can be probed. This is illustrated in Fig. 1 for the [210] direction where it is seen that for ΔK outside the first surface Brillouin zone several high-symmetry directions are accessed with significant components parallel to the SH polarization [for example, at the point where $\boldsymbol{Q}=2/3\bar{\Gamma}\bar{X}$, see Fig. 1(b)] and thus a significant coupling to SH modes is expected.

The TOF spectra were measured along the [210] direction between the M points, which lies in the positive and negative directions in the middle between the (0,0) and the (3,$\bar{1}$) Bragg peaks (see Fig. 1). Three representative TOF spectra, which have been converted to an energy transfer scale, are shown in Fig. 2. These TOF spectra are part of a measured collection of about 45 spectra taken over a wide incident angular range, Θ_i at intervals of 0.5°, with an incident wave vector near 6.24 Å^{-1} (incident energy $E_i=20.4$ meV). Each spectrum required approximately 30 min. The measured phonon frequencies and the corresponding phonon wave vectors were identified by Eq. (1) and used to construct the surface phonon dispersion curves. The measured phonon dispersion curves are plotted in Fig. 3 in an extended-zone diagram. Three scan curves corresponding to the TOF spec-

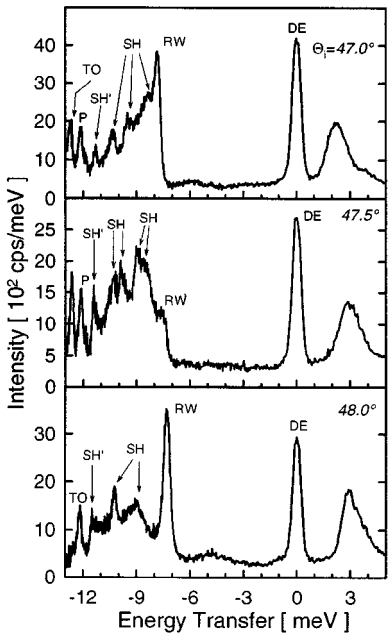

FIG. 2. Time-of-flight measurements converted to energy-loss spectra for NaCl(001)[210]. The incident wave vector $\boldsymbol{k}_i$ was 6.24 Å^{-1} and the substrate was at a temperature of 100 K. The peaks in the spectra labeled RW and SH (SH′) correspond to the Rayleigh and the shear-horizontal modes, respectively. The other peaks are identified in the text.

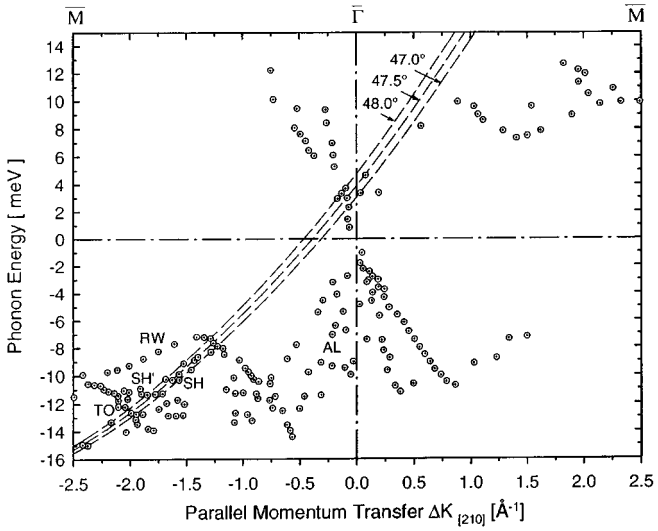

FIG. 3. Extended zone diagram of the measured dispersion curves for the [210] direction for NaCl(001) constucted from the TOF spectra. The scan curves calculated from Eq. (1) corresponding to the TOF spectra in Fig. 2 are also shown by the dashed lines and the peaks can be identified. Resonance peaks labeled (P) in Fig. 2 are not shown in the extended zone diagram.

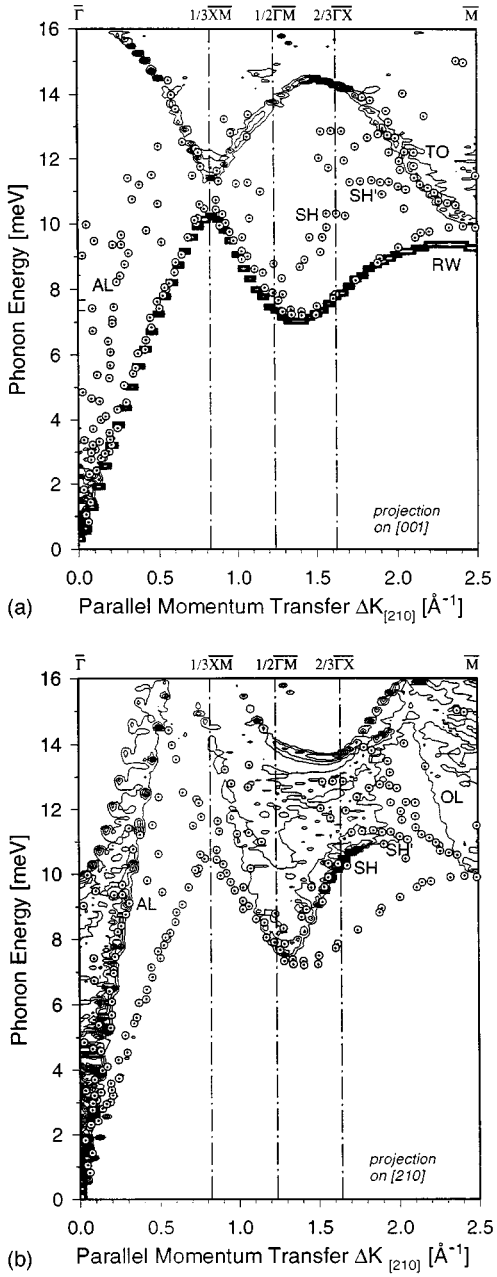

FIG. 4. Measured (open dotted points) and calculated dispersion curves (shown as contour plots) for the [210] direction for NaCl(001) as a function of parallel momentum transfer. The calculated curves represent the density of modes weighed with the square amplitude of oscillation and projected on the [001] (perpendicular to the surface) (a) and on the [210] direction (parallel to the surface) (b). In (a), the two transverse modes, the RW and the transverse optical (TO) modes are projected out, while in (b) the SH and SH′, the optical OL and the AL modes are projected out. The other labeled modes are discussed in the text. In both plots the contour line density is proportional to the calculated phonon density and, hence, the black regions have the highest density.

tra presented in Fig. 2 are also shown in Fig. 3. To conduct a theoretical analysis the measurements in the [210] direction were projected onto the positive energy and parallel wave-vector transfer side as shown by the identical set of dotted open circles in Fig. 4(a) and 4(b). For comparison see the density of states of phonons in the scattering plane shown as contour plots for normal polarizations [Fig. 4(a)] and in-plane polarizations along the [210] direction [Fig. 4(b)].

Since the measured surface dispersion curves in Fig. 4 are not distinguishable as to whether they are polarized perpendicular to the surface ([001]) or in the [210] direction a slab calculation based upon the breathing shell model[22,23] was performed to interpret the measured dispersion curves. Following the approach used for the Green's function method[23,24] a slab was constructed with cyclic boundary conditions starting from the dynamical matrix for the bulk. Perturbations to reestablish invariance were then introduced to take into account the effect of the surface and a calculation for a 200-layer slab along the $\langle 210 \rangle$ direction was performed. Contour plots were made of the surface phonon density weighted with the squared vibrational amplitude projected onto a direction normal to the surface [001] [Fig. 4(a)] and along the azimuthal direction of the measurements [Fig. 4(b)], respectively. The polarizations of the surface phonon modes are indicated in the calculated contour plots in Figs. 4(a) and 4(b) and are used to identify the measured data points. The evidence for the SH modes is found in Fig. 4(a) and 4(b) in the region of surface wave vector $\Delta K = 1.2$ to 2.0 Å^{-1} and phonon energy $\hbar\omega = 7$ to 10 meV. The contour plots for the [001] polarization in Fig. 4(a) definitely demonstrate that the mode with the lowest energy is polarized perpendicular to the surface and is the transverse acoustic Rayleigh wave (RW) mode. It is also seen from this figure that in the region where the phonon modes SH and SH′ are observed the density of phonons with the polarization perpendicular to the surface is negligible. However, a comparison of the experimental results with the calculated dispersion curves from Fig. 4(b), where the modes polarized along the [210] direction are presented, provides strong evidence that the higher energy mode can be attributed to the SH modes. The measured phonons around $\Delta K = 1.6$ Å^{-1} and phonon energy of 10 meV lie exactly at positions where phonons with shear-horisontal polarization are expected. This permits the interpretation of the points marked by SH and SH′ in Fig. 4 as SH modes. SH′ is used to mark a continuation of the SH mode at the region of higher energies. It should be noted that the SH mode has a pure SH polarization only at three points in the Brillouin zone shown in Fig. 4, namely at $1/3XM$, $1/2\Gamma M$, and $2/3\Gamma X$. Outside of these points the mode is no longer pure SH polarized because of a component with longitudinal polarization.

All phonon peaks in Fig. 2 assigned to the dispersion curves of Fig. 4 are labeled with the corresponding letters. To identify the other peaks in the phonon spectra we have performed a careful analysis of phonon-assisted selective adsorption resonances. These can also appear as sharp features in the TOF spectra.[25,16,26] The resonance curves[25] for the four bound states of He on NaCl (Ref. 14) and for different surface two-dimensional reciprocal lattice vectors exchanged in the resonance process were plotted in an extended surface Brillouin zone. This permitted the identification of the peaks in the TOF spectra corresponding to resonances and their subsequent removal from the dispersion curves presented in Fig. 4. The corresponding resonance peaks are labeled with (P) in the TOF spectra in Fig. 2.

In Fig. 2 peaks corresponding to both RW and SH modes are observed in the same spectra. As seen from Fig. 3, the scan curves [Eq. (1)] corresponding to the angles where the

TOF spectra from Fig. 2 were measured are nearly parallel to the SH phonon mode and intersect the SH mode many times resulting in multiple peaks in the TOF spectra related to this mode. The peaks corresponding to the mode SH′, which is an upper branch of the SH mode (Fig. 4), are also clearly seen in the TOF spectra. By comparing the measured and the calculated dispersion curves, the other modes in Fig. 4 labeled with OL (optical longitudinal) mode, TO (transverse optical) mode, and AL (acoustic longitudinal) mode can also be assigned.

IV. CONCLUSIONS

We believe that this is the first evidence for shear-horizontal modes measured by He scattering for an insulator surface. In the only other reported previous work Doak *et al.*[13] found no evidence for SH modes on LiF. The present work clearly demonstrates that the shear-horizontal mode has a strong experimental signature. It further illustrates that by moving the sagittal plane away from the high symmetry directions by an azimuthal angle ϕ provides a simple way to explore the shear-horizontal polarized surface phonons. The results agree well with theoretical calculations for the dispersion curves determining the location of the SH mode.

Finally, the epitaxial growth of one alkali halide on another alkali halide has been investigated by elastic and inelastic helium atom scattering in the high symmetry directions.[27,28] Mostly, only the perpendicular and dispersionless modes that lie in the sagittal plane have been measured as a function of growth. As a result of the present work, the SH mode should also be accessible to study as a function of coverage. A promising system is KBr/NaCl(001) (Ref. 27) since, for the clean NaCl surface, the frequency at the X point for the SH mode as found here is $1.91\text{x}10^{13}$ rad/s. As the number of layers increases approaching the surface of pure KBr crystal, this frequency is predicted to drop to 1.28×10^{13}rad/s.[29] This large change should be observable and provide guidance on the in-plane strain during the growth process. It also provides an additional test on the usefullness of the shell model for describing the transition in dynamic behavior during growth. Deviations from the theory would then provide evidence for strain.[30]

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[1] G. Brusdeylins, R.B. Doak, and J.P. Toennies, Phys. Rev. Lett. **44**, 1417 (1980).
[2] J.P. Toennies, in Chap. 5 of *Surface Phonons*, edited by W. Kress and F.W. de Wette (Springer, Berlin, 1990).
[3] G. Boato, in *Atomic and Molecular Beam Methods*, edited by G. Scoles (Oxford University Press, New York, 1992), Vol. 2, pp. 340–365.
[4] R. B. Doak, in *Atomic and Molecular Beam Methods* (Ref. 3), pp. 384–443.
[5] R. E. Allen, G. P. Alldrege, and F. W. de Wette, Phys. Rev. B **4**, 1648 (1971).
[6] G. P. Alldredge, Phys. Lett. **41A**, 281 (1972).
[7] M. Balden, S. Lehwald, H. Ibach, A. Ormeci, and D.L. Mills, Phys. Rev. B **46**, 4172 (1992).
[8] J.A. Stroscio, M. Persson, S.R. Bare, and W. Ho, Phys. Rev. Lett. **54**, 1428 (1985).
[9] J.E. Yater, A.D. Kulkarni, F.W. de Wette, and J.L. Erskine, J. Electron. Spectrosc. Relat. Phenom. **54/55**, 395 (1990); J.L. Erskine and E.-J. Jeong, J. Vac. Sci. Technol. A **8**, (1990) 2469.
[10] J.L. Wilkes, R.E. Palmer, and R.F. Willis, J. Electron. Spectrosc. Relat. Phenom. **44**, 355 (1987).
[11] C. Oshima, T. Aizawa, R. Souda, Y. Ishizawa, and Y. Sumiyoshi, Solid State Commun. **65**, 1601 (1988).
[12] K.-M. Martini, Ph.D. thesis, Boston University, 1986.
[13] R. B. Doak, Superlattices Microstruct. **7**, 201 (1990).
[14] G. Benedek, G. Brusdeylins, R. B. Doak, J. G. Skofronick, and J. P. Toennies, Phys. Rev. B **28**, 2104 (1983).
[15] G. Benedek, Phys. Rev. Lett. **35**, 234 (1975).
[16] S. A. Safron, W. P. Brug, G. Chern, J. Duan, and J. G. Skofronick, J. Vac. Sci. Technol. A **8**, 2627 (1990); S. A. Safron, W. P. Brug, G. G. Bishop, G. Chern, M. E. Derrick, J. Duan, M. E. Deweese, and J. G. Skofronick, *ibid.* **9**, 1657 (1991).
[17] G. Benedek, A. Glebov, W. Silvestri, and J.G. Skofronick, J. Vac. Sci. Technol. A **14**, 1522 (1996).
[18] J. P. Toennies and R. Vollmer, Phys. Rev. B **44**, 9833 (1991).
[19] G. Brusdeylins, R. B. Doak, and J. P. Toennies, Phys. Rev. B **27**, 3662 (1982).
[20] J. P. Toennies and K. Winkelmann, J. Chem. Phys. **66**, 3965 (1977).
[21] Karl Korth Kristalle GmbH, Am Jägersberg 3, D-24161 Altenholz (Kiel), Germany.
[22] U. Schröder, Solid State Commun. **4**, 347 (1966); U. Schröder and V. Nüsslein, Phys. Status Solidi **21**, 309 (1967).
[23] G. Benedek, Phys. Status Solidi B **58**, 661 (1973); Surf. Sci. B **61**, 603 (1976).
[24] G. Benedek and L. Miglio, in *Surface Phonons*, edited by W. Kress and F. W. de Wette (Springer-Verlag, Berlin, 1991).
[25] D. Evans, V. Celli, G. Benedek, J. P. Toennies, and R. B. Doak, Phys. Rev. Lett. **50**, 1854 (1983).
[26] G. Benedek, R. Gerlach, A. Glebov, G. Lange, S. Miret-Artes, J. G. Skofronick and J. P. Toennies, Phys. Rev. B **53**, 11 211 (1996).
[27] S. A. Safron, G. G. Bishop, J. Duan, E. S. Gillman, J. G. Skofronick, N. S. Luo, and P. Ruggerone, J. Phys. Chem. **97**, 2270 (1993).
[28] S. A. Safron, J. Duan, G. G. Bishop, E. S. Gillman, and J. G. Skofronick, J. Phys. Chem. **97**, 1749 (1993).
[29] W. Kress, F. W. de Wette, A. D. Kulkarni, and U. Schröder, Phys. Rev. B **35**, 5783 (1987).
[30] E. S. Gillman, J. Baker, J. J. Hernandez, G. G. Bishop, J. A. Li, S. A. Safron, J. G. Skofronick, U. Schröder, and D. Bonart, Phys. Rev. B **53**, 13 891 (1966).