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Calculation of phonon dispersion on the ZnSe(110) surface

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We have studied surface phonons on ZnSe(110) using the adiabatic bond-charge model. The structural and electronic information necessary for these calculations is taken from a self-consistent pseudopotential calculation. We have presented a discussion on the location and polarization of surface phonon modes at the symmetry points of the surface Brillouin zone. We have also compared the results for surface phonons on this surface with those on the III-V(110) surfaces. [S0163-1829(98)05904-9]

Although the (110) surface of zinc-blende binary compounds has been among the most widely explored, most experimental and theoretical studies have been devoted to a determination of atomic geometry and electronic states. The atomic geometry of the ZnSe(110) surface were determined using low-energy electron diffraction[1] and elastic low-energy electron diffraction,[2] while surface electronic bands have been mapped by angle-resolved photoemission.[3] On the theoretical side, the atomic geometry of this surface was studied using a tight-binding model[4] and a self-consistent pseudopotential calculation.[5]

While He-atom scattering[6] and high-resolution electron-energy-loss spectroscopy[7] have been used to study surface-phonon modes of some III-V(110) surfaces, no experimental work has been done on the surface-phonons of II-VI(110). On the theoretical side, only a rotational surface-phonon mode for ZnSe(110) has been identified by using a tight-binding total-energy scheme.[8] Lattice-dynamical considerations are important in determining the electron-phonon interactions, and also provide a hitherto somewhat neglected probe of surface structure.

Recently, the adiabatic bond-charge model (BCM) was successfully applied to study the bulk-phonon dispersion curves of II-VI compounds.[9] Moreover, we showed that the adiabatic bond-charge model as a reliable theoretical technique for the description of the surface dynamics of III-V(110).[10–14] Thus, due to structural similarities between II-VI(110) and III-V(110) surfaces, we applied the BCM to the ZnSe(110) surface. The structural and electronic information necessary for these calculations is taken from self-consistent pseudopotential calculation.[5] The polarization and localization of vibrational modes along symmetry directions on the surface Brillouin zone are discussed. We find that the surface dynamics of ZnSe(110) is characterized by the presence of a rotational mode at the zone center, three acoustic modes at a zone edge, and the Fuchs-Kliewer mode at the zone center, similar to what is found for III-V(110) (Ref. 13) in general, and for GaAs(110) (Ref. 10) in particular.

For BCM calculations, we modeled the ZnSe(110) surface in a repeated slab scheme, similar to that used for plane-wave pseudopotential calculations of atomic geometry and electronic states. The supercell consisted of 11 layers of ZnSe and a vacuum region equivalent to nine atomic layers. Atoms in the top three layers on each side are placed at their relaxed positions obtained from a self-consistent pseudopotential calculation,[5] while deeper-lying atoms are taken at their bulk positions. The relaxed surface is characterized by fully occupied Se dangling bonds and completely empty Zn dangling bonds. The position of the Se dangling bond charge (BC) is obtained from the maximum valence electron density, and is indicated in Fig. 1.

In order to apply the BCM to the ZnSe(110) surface, we considered three types of interactions:[9,10] (i) the Coulomb interaction, which acts between all particles (ion-ion, ion-BC, and BC-BC), is controlled by the model parameter Z^2/ε,

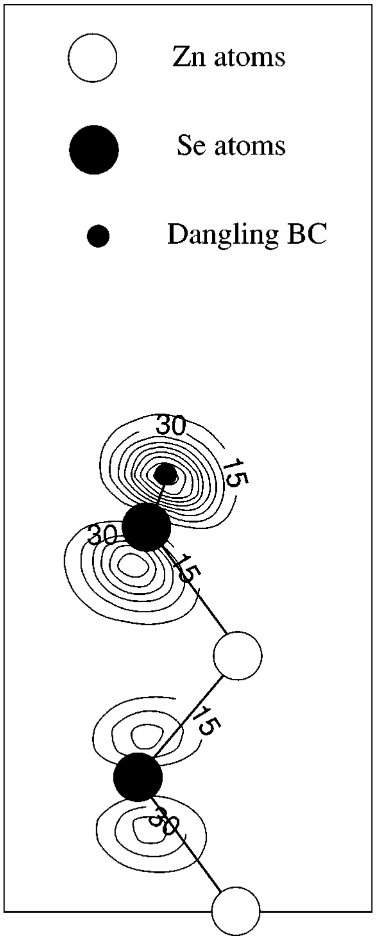

FIG. 1. Electronic charge density for the dangling bond charges on ZnSe(110). The position of the dangling bond charge (BC) is indicated.

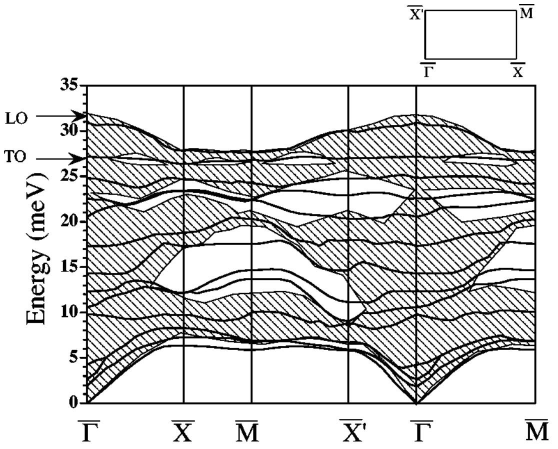

FIG. 2. The dispersion of surface-phonon modes on the ZnSe(110) surface. The calculated results for the are shown by thick solid curves, while the projected bulk ZnSe phonon energies are shown by hatched regions.

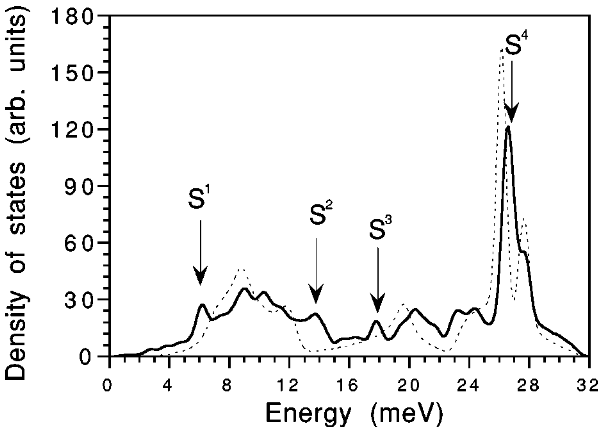

FIG. 3. The density of phonon states on the ZnSe(110) surface. The solid curve is obtained from the (110) slab supercell calculation with the relaxed geometry, while the dotted curve shows the density of states of bulk ZnSe.

with ε the dielectric constant, (ii) a central two-body potential acting between nearest-neighbor particles (i.e., between ion-ion, ion-BC, and BC-BC); and (iii) a bond-bending potential of the Keating form, involving the BC-ion-BC angle. The surface BCM parameters have been redefined to achieve equilibrium conditions by invoking translational and rotational invariance throughout the supercell.[10,11,13]

The phonon-dispersion curves for the (110) surface of ZnSe are shown in Fig. 2. Due to the small cation-anion mass difference in ZnSe, there exits no energy gap between the bands of the acoustic and optical bulk phonons. In Fig. 3 the phonon density of states of ZnSe(110) is shown together with the phonon density states of bulk ZnSe. The peaks labeled S^1–S^4 are dominated by atomic vibrations on the surface. Peak S^1 at around 6 meV mainly results from surface acoustic phonons along the $\overline{X}$-$\overline{X'}$ direction (see Fig. 2). The second peak S^2 at around 13.5 meV is characterized by surface-optical-gap-phonon modes in the lowest-lying stomach gap region along the $\overline{X}$-$\overline{M}$ and $\overline{\Gamma}$-$\overline{M}$ directions (see Fig. 2). Peak S^3 originates from surface phonons along the $\overline{\Gamma}$- $\overline{X'}$ and $\overline{X}-\overline{M}$ directions. Peak S^4 at around 27 meV is also characterized by atomic vibrations on the surface. This peak corresponds to the flat phonon modes along the surface Brillouin zone, as seen in Fig. 2.

Atomic vibrations along $[1\overline{1}0]$, i.e., along the III-V zigzag chain direction, are represented as A'' modes, and vibrations perpendicular to the chain direction are represented as A'. Such a clear classification is not possible along the symmetry directions $\overline{\Gamma}$-$\overline{X}$ and $\overline{\Gamma}$-$\overline{M}$ on the surface Brillouin zone. Along these directions modes show a mixture of shear-horizontal and saggital-plane polarizations.

In Table I we list the calculated frequencies and polarization characters of some of the surface modes at the $\overline{\Gamma}$ point. For comparsion, in Table I we also list a few A'' and A' phonon modes on a number of III-V(110) surfaces. Clearly, the ZnSe(110) surface is characterized by the presence of modes similar to those on III-V(110). Figure 4 shows the displacement pattern for the rotational, bond stretching, and Fuchs-Kliewer modes at 9.80, 17.31, and 30.90 meV, respectively. Our calculated rotational mode at 9.80 meV can be compared with a similar mode at 11.7 meV obtained in the work by Wang and Duke.[8] The bond-stretching phonon mode at 17.31 meV is due to the first layer atoms vibrating against each other in the [001] direction. The Fuchs-Kliewer mode at 30.90 meV corresponds to the first- and second-layer Zn atoms vibrating against the first- and second-layer Se atoms, with the second- and third-layer atoms making a significant contribution. Such an observation has also been made for the GaAs(110) surface.[10] In a previous paper,[13] we showed shown that the effective force constant for the Fuchs-Kliewer mode on III-V(110) surfaces is very similar, and the difference in the energy of this mode is mainly due to the reduced mass difference. Although the reduced mass

TABLE I. Calculated surface-phonon frequencies (in meV) of ZnSe(110) at the $\overline{\Gamma}$ point. We also compare these results with those on the III-V(110) surfaces. RM, BS and FK indicate the rotational mode, bond-stretch mode, and Fuchs-Kliewer frequency, respectively.

Surfaces	A'' modes			A' modes					
ZnSe(110)	10.57	20.55	27.18	9.80	14.30	17.31	22.55	24.83	30.90
GaAs(110) (Ref. 10)	11.95	28.86	32.18	10.99		22.80			35.80
InP(110) (Ref. 11)	10.10	31.03	46.68	9.10		28.13			43.30
GaP(110) (Refs. 12 and 13)	16.54	38.79	41.51	14.53		35.13			49.69
InAs(110) (Refs. 13 and 14)	10.33	25.85	28.74	9.29		20.82			29.50
				RM		BS			FK

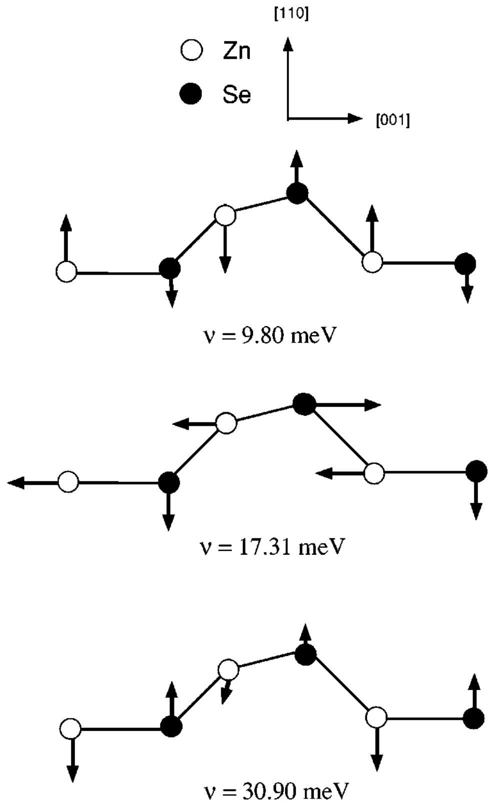

FIG. 4. Atomic displacement patterns of selected surface-phonon modes at the $\bar{\Gamma}$ point.

and lattice constant of ZnSe and GaAs are very close to one another, there is a significant difference in their Fuchs-Kliewer frequencies. This difference is due to the difference in the bulk force-constant parameters and ionicities of these surfaces.

As we modeled the surface in a repeated slab geometry, our calculations also yield plate modes. Such modes appear as Lamb waves[15] [polarized in the saggital (SP) plane] and Love waves[16] [polarized in the shear horizontal (SH) plane]. The Lamb waves can further be categorized as asymmetric [SP(a)] and symmetric [SP(s)] with respect to the middle of the slab. As an example, at the $\bar{\Gamma}$ point we have calculated a SH mode at 1.85 meV, a SP(a) mode at 2.64 and a SP(s) mode at 4.25 meV. (We have investigated their polarization characteristics at points slightly away from the $\bar{\Gamma}$ point.) The symmetry-related partners of these SP(a) and SP(s) Lamb waves correspond to the zero frequency. The energies of these plate modes are dependent upon the thickness of the slab. In agreement with this we observed the above three phonon modes at 1.05, 1.49, and 2.37 meV with 20-layer-thick slabs. All other phonon frequencies presented in this paper, other than these three, are well converged with respect to the slab thickness.

The ZnSe(110) surface exhibits three surface-acoustic-phonon modes at $\bar{X}'$, as found an III-V(110) surfaces[13]. These are predicted at energies of 5.85, 5.91, and 6.74 meV. The intermediate phonon mode is characterized by a pure shear-horizontal displacement pattern, while the other two are dominated by a pure saggital displacement pattern. The highest surface-optical-phonon mode at 30.07 meV has the same displacement pattern as found on III-V(110) surfaces.[13]

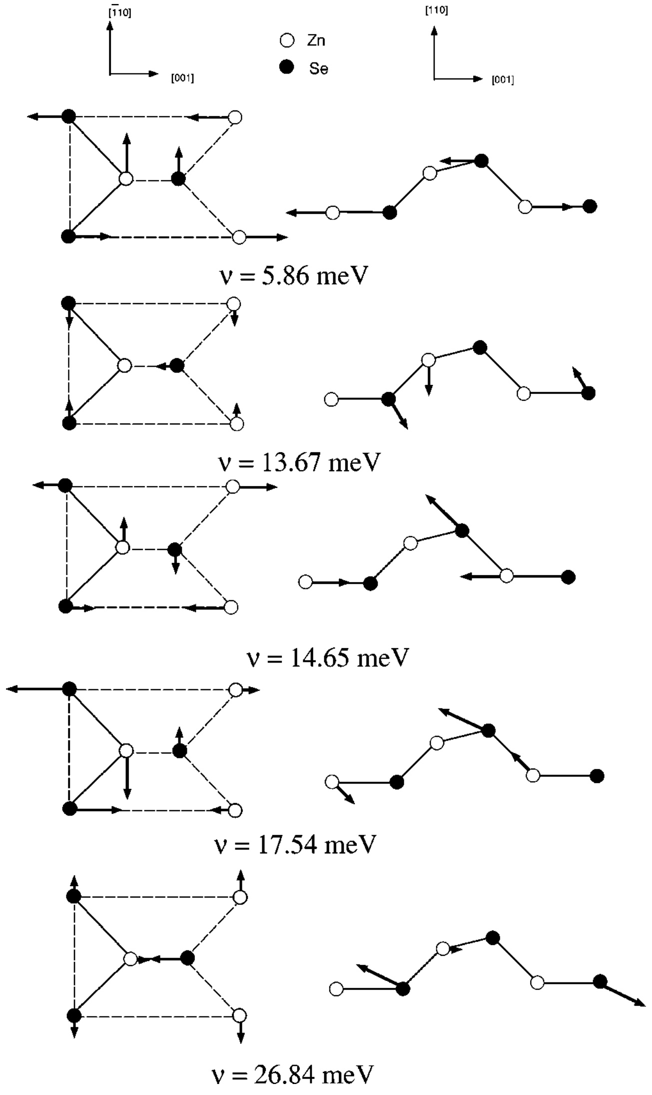

FIG. 5. Atomic displacement patterns of selected surface-phonon modes at the $\bar{M}$ point.

The Rayleigh wave (RW) phonon mode at 6.35 meV at $\bar{X}$ has a different polarization character from that on the GaAs(110) surface. This phonon mode on GaAs(110) (Refs. 10 and 13) is nearly totally polarized as a SP, while it has 58 % SP character for ZnSe(110). This phonon mode is due the motion of top-layer Se atoms and second-layer Zn atoms with components in both the [110] and [001] directions for the ZnSe(110) surface, while it is characterized by the vibrations of top-layer Ga and second-layer As atoms along the [110] direction for GaAs(110). The highest surface-optical-phonon mode at 27.81 meV is due to the motion of second-layer Zn atoms with components in both the [110] and [001] directions, while the second-layer Se atoms displace in zigzag chain direction.

Atomic displacement patterns of selected surface-phonon modes at the $\bar{M}$ point are presented in Fig. 5. The RW frequency at at 5.86 meV is due to the motion of first-layer Zn and second-layer Se atoms in the zigzag chain direction, while the first-layer Se and second-layer Zn atoms vibrate in the [001] direction. The frequencies at 13.67, 14.65, and 17.54 are truely localized surface-phonon modes in the lowest stomach gap region. In the same frequency range, we also found three surface modes on GaAs(110),[10] two of which are resonant with the bulk spectrum below the stomach gap. At this symmetry point the highest surface-optical-phonon mode at 27.64 meV comes from the motion of third-layer atoms, with Zn atoms vibrating with components in both the [110] and [001] directions, and Se atoms vibrating in the zigzag chain direction.

In conclusion, we reported the application of the adiabatic bond-charge model in the calculation of phonon modes on the ZnSe(110) surface. The relaxed atomic geometry and dangling BC positions were taken from a self-consistent pseudopotential calculation. We presented a detailed account of phonon frequencies and polarization of atomic vibrations along various symmetry directions on the surface Brillouin zone for this surface. The rotational phonon mode predicted by Wang and Duke can be identified in or work, and in general it is found that this surface shows dynamical behavior similar to III-V(110) surfaces.

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