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Phonons at III–V (110) surfaces

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Abstract

We have applied the ab initio pseudopotential frozen phonon approach to study phonon frequencies and eigenmodes for III–V (110) surfaces. For GaAs our results at the $\bar{\Gamma}$ and $\bar{X}$ points are in good agreement with data from recent HREELS and He scattering experiments. In the energy range of the controversially discussed A_1 mode we observe a rotational surface phonon with substantial bulk contributions. Calculations for surface $\bar{\Gamma}$ phonons of InAs, GaP and InP show that energy shifts and displacement patterns are strongly correlated with constituent atomic masses.

Keywords: Density functional calculations; Molecular dynamics; Phonons; Gallium arsenide; Gallium phosphide; Indium arsenide; Indium phosphide; Low index single crystal surfaces

In recent years a number of studies on the vibrational properties of GaAs(110) surfaces have been published. However, the results do not present a clear picture. One of the key points of the current discussion concerns the existence and nature of the so-called A_1 mode detected with inelastic He atom scattering [1]. This mode has a relatively low intensity and forms a rather flat band at 10 meV between $\bar{\Gamma}$ (centre of surface Brillouin zone (SBZ)) and $\bar{X}$ (zone boundary along $[1\bar{1}0]$). A more intense mode, called A_2, was found at 13 meV near $\bar{X}$. Higher energies have been studied using high resolution electron energy loss spectroscopy (HREELS) with reports of two $\bar{\Gamma}$ modes at energies 17.5 and 23.2 meV [2]. In several HREELS studies [2,3] a Fuchs–Kliewer, or surface optical, phonon at an energy between 35.0 and 36.2 meV has been detected. A recent HREELS study by Nienhaus and Mönch [4] examines the GaAs(110) surface phonons throughout the SBZ. Besides two acoustic surface phonon branches with energies lower than 9 meV they find four almost flat phonon bands near 10.5, 16.5, 21.5, and 35.8 meV.

A variety of theoretical techniques have been applied to the GaAs(110) surface dynamics. From a tight-binding (TB) calculation Wang and Duke [5] interpreted the A_1 mode as a rotational surface phonon involving the top layer atoms. A later TB study [6] reports a pure horizontal polarization of A_1 at the $\bar{\Gamma}$ point. However, if the latter is true then the A_1 mode should not be detectable by He scattering. Bond charge model calculations [7] report the A_1 mode to be a true surface state near the zone boundary which develops into a broad resonance at the zone centre. Utilizing a TB total energy model Godin et al. [8] find a surface $\bar{\Gamma}$ phonon at 9.3 meV which

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corresponds to a chain bouncing mode. This has been confirmed by a later TB molecular dynamics simulation [9]. Di Felice and coworkers [10] used an ab initio molecular dynamical approach to determine vibrational modes at high symmetry k points in the SBZ. They noticed some surface related features mixed with bulk states at an energy of about 11 meV. Fritsch et al. [11] employed an ab initio linear response approach to calculate the full phonon dispersion of GaAs(110) along $\overline{\Gamma X}$ and $\overline{\Gamma X'}$. They did not find a surface state explaining the A_1 mode, but observed a broad feature around 10 meV arising from a series of states which deeply penetrate into the bulk.

The aim of our study is to contribute to the understanding of the surface dynamics of the III–V (110) surfaces. We use an ab initio pseudopotential method based on the frozen phonon approach to calculate the surface phonons modes and frequencies for GaAs(110) at $\bar{\Gamma}$ and $\bar{X}$. In the $\bar{\Gamma}$ case the frequencies and eigenvectors are compared with surface phonons calculated for the (110) surfaces of InAs, GaP and InP. The pseudopotential method is based on density functional theory (DFT) within the local density approximation (LDA). Details of the calculation are given in Refs. [12–14]. We start from the fully relaxed III–V (110) surface geometries determined in perfect agreement with Ref. [15]. In an earlier publication [13] it was shown that the dynamical properties of crystalline surfaces can be reliably described by using a simple restricted dynamical model. We follow that approach, but consider a larger dynamical problem, using a 2×1 surface unit cell for GaAs(110) in order to calculate both the $\bar{\Gamma}$ and the $\bar{X}$ phonons. The eigenvalues and eigenvectors were obtained by diagonalizing the matrix equation,

$$\boldsymbol{M\ddot{u}} = \boldsymbol{Ku} \tag{1}$$

where $\boldsymbol{M}$ represents the vector of the atomic masses. The elements $k^{ij}_{\alpha\beta}$ of the dynamical matrix $\boldsymbol{K}$ were obtained by displacing atom i from its equilibrium position in the direction α and calculating the force acting on atom j in the direction β. Thereby α, $\beta = (x,y,z)$ and $i,j = 1,N$, where N is the number of atoms in the uppermost three layers. From the obtained eigenvectors and eigenvalues those which are localized at the surface were compared with experiment.

Results of our calculation on GaAs(110) are compiled in Tables 1 and 2. In these tables a comparison is given with recently published results. The eigenfrequencies have been ordered according to their displacement pattern as far as those were given in the references. We have only selected the modes that describe a more or less pronounced surface character. Our results are set in round brackets when the displacements of the outermost anions and cations contribute less than 50% to the total of the atomic displacements.

The surface phonons at $\bar{\Gamma}$ can be classified according to the irreducible representations of the point group of the surface unit cell: A″ modes describe lattice distortions along the III–V zigzag chains,

Table 1
Comparison of calculated surface phonon frequencies of GaAs(110) at $\bar{\Gamma}$ with earlier calculations and experiments

	Mode								
	A′						A″		
Present results	(11.1)	14.6	(17.7)	23.2		35.8	(8.6)	31.1	31.7
[Dipole]	[0.2]	[0.3]	[0.1]	[0.1]		[1.5]	[0.0]	[0.0]	[0.0]
Ab initio [11]		16.2		23.7	30.9	34.6		30.0	32.2
Ab initio [10]	11.0	13.3			27.3	34.1			
He scattering [1]	10.0								
HREELS [2]			17.5	23.2		35.0			
HREELS [4]	10.5		16.5	21.1		35.8			

Frequencies $\hbar\omega$ are given in meV.
Results in round brackets describe displacement patterns with relatively weak surface localization.
The normalized change of the macroscopic surface dipole potential due to the specific distortion pattern is given in square brackets.

Table 2
Comparison of calculated surface phonon frequencies $\hbar\omega$ (in meV) of GaAs(110) at $\bar{X}$ with earlier calculations and experiments

	Mode									
	Rayleigh		Other acoustic and optical modes							
Present results	8.7	8.9	(11.1)	13.0	14.2	22.7		28.2	32.0	35.5
Ab initio [11]	8.6	8.9		13.0	14.5			27.4		34.4
Ab initio [10]	4.4	8.8	11.0		13.6	22.3	22.9		30.0	33.5
He scattering [1]	8.3		10.0	13.0						
HREELS [4]	8.6				14.8	21.5				36.2

Results in round brackets describe displacement patterns with relatively weak surface localization.

whereas A′ modes correspond to atomic displacements perpendicular to the chain direction. Such a clear classification of modes is impossible at $\bar{X}$: since the sagittal plane defined by the surface normal and the wave vector is not a reflection plane, the displacement patterns do not show clear polarization properties.

Not all modes described in our and earlier calculations have been detected experimentally. One reason could be low scattering efficiency for some modes. In particular A″ modes represent shear horizontal motions that cannot be detected by HREELS or He atom scattering. On the other hand some states which cannot be identified as clearcut surface phonons seemingly have large scattering efficiency and are therefore detected in experiments. However, there are also theoretical difficulties in clearly identifying surface and bulk-like modes: Within the slab approach and the restriction to a few atomic layers which are allowed to vibrate only surface phonons may be reasonably described.

The two lowest energies shown in Table 2 correspond to surface acoustic displacement patterns. They are energetically very close and therefore probably cannot be resolved in scattering experiments. We find the lower energy mode to be characterized by an in-phase vibration of the first layer As atoms and second layer Ga atoms perpendicular to the surface. The higher energy mode possesses a complementary character which is also reported in Refs. [10,11]. Both phonons have displacement vectors which are partly in the sagittal plane and can therefore be understood as Rayleigh waves although there is some confusion in the literature concerning their notation.

The surface A_1 phonon branch found at about 10 meV at the $\bar{\Gamma}$ point [1,4] should have A′ symmetry. At 11.1 meV we find an A′ phonon which is best described as a rotational mode of the GaAs chains at the surface (cf. Fig. 1a). Although there is an appreciable contribution of the outermost surface atoms we observe considerable displacements of the atoms in the deeper layers and therefore would not classify this mode as a surface phonon. However, our result is in surprisingly good agreement with an earlier work by Wang and Duke [5] who predicted a frequency of 10.7 meV corresponding to the rotation of the top layer GaAs chain. Rather similar is the

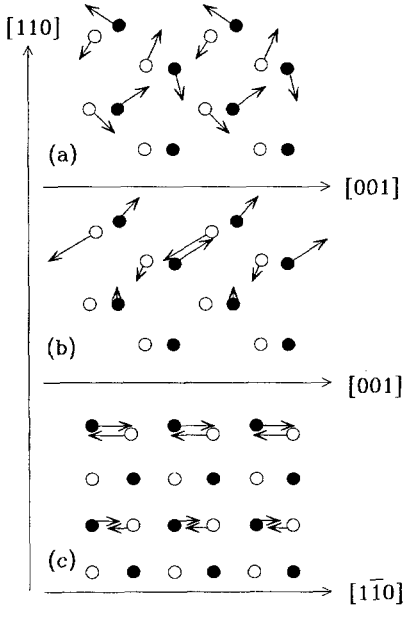

Fig. 1. Displacement pattern of the surface $\bar{\Gamma}$ phonons of GaAs(110): (a) and (b) show the A′ modes at 11.1 and 35.8 meV, (c) shows the A″ mode at 31.7 meV. White (black) circles denote the cations (anions).

situation at $\overline{X}$. There we find two states which are energetically rather close at 11.1 meV and show some localization at the surface. They belong to complementary displacements as one mode is mainly localized at the surface anion and the second layer cation and the other at the surface cation and the second layer anion.

The $\overline{\Gamma}$ phonon at 14.6 meV is mostly localized on the top layer Ga atom. Experimentally a so-called A_2 mode has been detected at $\overline{X}$ at 13 meV. At this energy we find a vibrational state dominated by the displacements of the first layer Ga ions in the chain direction and of the uppermost As ions perpendicular to the surface chains.

At 17.7 meV we observe a state which at $\overline{\Gamma}$ is mainly localized at the anions in the top and second layers, which move against each other along the surface normal. However second and third layer cations also contribute to that mode. In this energy range the HREELS experiments [2,4] measured a weak energy loss. At the zone boundary ($\overline{X}$) we find a surface phonon at 14.2 meV strongly localized at the outermost cation: The first layer Ga atoms vibrate perpendicular to the plane defined by the first and second layer As atoms.

A surface phonon is also detected experimentally [2,4] between 21 and 23 meV. At $\overline{\Gamma}$ we calculate a horizontal [001] shear mode of the top layer GaAs chain with some vertical contribution from deeper layers with an energy of 23.2 meV. At $\overline{X}$ this mode lies at a slightly lower energy of 22.7 meV and is dominated by horizontal vibrations of the top layer As combined with a vertical motion of the Ga in the second layer.

We find a mode describing a bond stretching between first layer cation and second layer anion (cf. Fig. 1b) at 35.8 meV. In Table 1 the change in the macroscopic dipole potential of the GaAs(110) surface caused by the specific displacement pattern is given. We find that for the A′ optical phonon at 35.8 meV the change of the surface dipole is much more pronounced than for any other surface phonon. This supports the identification of this mode as Fuchs–Kliewer phonon. The net dipole with a strong normal component associated with this phonon becomes obvious from Fig. 1b. We would like to point out that a mode with a similar substrate displacement pattern has been found for monolayer antimony covered III–V (110) surfaces. These modes, called 6A′ in Ref. [13], lie nearly at the same energy as the Fuchs–Kliewer phonons for the corresponding clean surfaces. This agrees with HREELS experiments, which show that the energy of GaAs(110) and InP(110) Fuchs–Kliewer phonons is only little effected by Sb deposition [16].

In order to deduce a chemical trend for the dynamical properties of III–V (110) surfaces we have also performed calculations of the surface $\overline{\Gamma}$ phonons of InAs, GaP and InP. The results are summarized in Table 3. The eigenfrequencies are ordered according

Table 3
Comparison of calculated surface phonon frequencies $\hbar\omega$ (in meV) on III–V (110) surfaces at $\overline{\Gamma}$ with earlier calculations and experiments

	Mode											
	A′							A″				
InAs	(8.0)	10.6	(15.8)		21.8	(24.3)	31.1	(5.9)	(7.4)		(28.4)	(28.8)
Ref. [5]	7.7											
Ref. [3]						29						
GaAs	(11.1)	14.6	(17.7)	23.2			35.8	(8.6)			31.1	31.7
Ref. [2,3]							35.0–36.2					
InP	(10.2)	12.1	(18.6)		34.2	36.0	46.7	(7.4)	(9.3)	(41.8)		43.6
Ref. [5]	7.8											
Ref. [3]							41.8–42.0					
Ref. [17]	10		17–20		30–32		42.5					
GaP	(14.6)	16.8			36.4	37.2	49.8	(10.8)	(13.2)		(45.0)	45.9
Ref. [5]	12.0											
Ref. [3]							48.0–49.1					

Results in round brackets describe displacement patterns with relatively weak surface localization.

to the symmetry of the displacement patterns and set in round brackets when they do not describe a clearcut surface phonon. However, before comparing our results with experiment a word of caution is necessary. Earlier DFT-LDA calculations for InAs and InP gave rise to a distinct underestimation of the lattice constant [15] and a corresponding overestimation of the bulk TO(Γ) frequency [13,14]. Also, for InAs and InP surfaces we find an overestimation of the calculated phonon frequencies by a few meV. Nevertheless, while the values for the In compounds are quantitatively not as reliable as for GaAs and GaP, they might at least be useful for discussing qualitative trends.

The force constant matrices of the four systems are rather similar and therefore of minor influence in governing a chemical trend. Thus the most important trend for the phonon frequency and atomic displacement pattern on III–V (110) is provided by the constituent masses. The Fuchs–Kliewer phonon is a good example for this statement. As shown in Fig. 1b this phonon describes a bond stretching between first layer cations and second layer anions. The character of the mode remains the same for the other considered surfaces. Only the magnitudes of the displacements vary: the relative amplitudes of the cation and anion motion in the top two surface layers are nearly proportional to their inverse mass ratio. The frequency of this phonon shows an almost linear correlation with the square root of the inverse reduced mass of the surface cation and anion (see Ref. [14]). A similar trend with the masses is found for the highest energy A″ phonons. These modes are dominated by a horizontal shear motion of the uppermost III–V chain along [1$\bar{1}$0] (cf. Fig. 1c). Their frequencies steadily increase if one goes to compounds with lighter reduced mass. The magnitude of the displacement of the individual atoms is strongly correlated to the inverse atomic masses. The degree of localization of this phonon also changes accordingly. For GaP and InP we find a strong surface character, whereas in GaAs and InAs there is also a considerable contribution from deeper layers. The main difference between the four compounds considered here is the appearance of a pronounced frequency gap between acoustic and optical vibrations for InP, InAs, and GaP due to the larger mass differences between anions and cations than in the

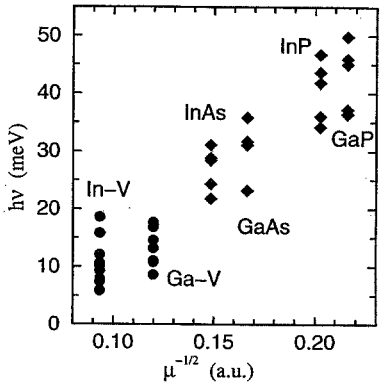

Fig. 2. Calculated frequencies of surface phonons (given in Table 3) are plotted versus the square root of the inverse mass. For optical modes (black diamonds) the reduced masses are taken, whereas for acoustic modes (black circles) the square root of the respective inverse cation mass is considered.

case of GaAs. Consequently, for instance, the A′ modes of InP at 34.2 and 36.0 meV are more localized at the surface than the 23.2 meV mode for GaAs. They fall into the mentioned energy gap and, therefore, represent true surface bound states.

The more complex the distortion patterns get, the more difficult it becomes to discuss the similarities and trends. In general we observe the trend towards higher surface phonon frequencies when considering compounds with lighter reduced mass. The validity of a corresponding description within the mass approximation, where only the masses vary, is demonstrated in Fig. 2. There the frequencies given in Table 3 are plotted either versus the square root of the cation mass (for acoustic modes) or versus the reduced mass (for optical vibrations). Here we use the bulk LA(X) frequencies of the compounds as criteria to discriminate between acoustic and optical modes. We observe an overall linear behaviour.

Altogether we find all surface phonons observed experimentally rather reliably reproduced in our calculation. The controversially discussed A_1 mode at GaAs(110) can be described as a rotational phonon of the surface zigzag chains. However, the localization of this mode at the surface is rather weak and does not justify a clear classification as a surface phonon. The excitation of the eigenmode with the highest frequency at $\bar{\Gamma}$ gives rise to a remarkable change of the electrostatic surface dipole and has therefore been identified as the Fuchs–Kliewer

phonon. Comparing the results for GaAs with those for other compound semiconductors, viz. InAs, GaP, and InP, we find that the force constant matrices of all the considered surfaces are rather similar, indicating the validity of the mass approximation. Energy shifts and changes in the displacement patterns are found to be strongly correlated to reduced atomic masses of the constituents of the materials. The bulk phonon band structures play only a minor role for the localization properties of surface phonons.

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