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III-V(110) surface dynamics from an *ab initio* frozen-phonon approach

W.G. Schmidt and F. Bechstedt
Friedrich-Schiller-Universität, Institut für Festkörpertheorie und Theoretische Optik, Max-Wien-Platz 1, 07743 Jena, Germany

G.P. Srivastava
Physics Department, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom

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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 $\overline{\Gamma}$ and $\overline{X}$ points are in good agreement with data from recent high-resolution electron-energy-loss spectroscopy and He-scattering experiments. In the energy range of the controversially discussed A_1 phonon we observe an eigenmode with large atomic amplitudes at the surface, which, however, is mixed with bulk states. In order to investigate the chemical trend, additional calculations for surface $\overline{\Gamma}$ phonons of InAs, GaP, and InP are presented. We observe a rather similiar dynamical behavior for all these surfaces with modifications mainly due to the different masses of group-III and -V elements.

I. INTRODUCTION

The clean GaAs(110) surface certainly belongs to the most intensively studied crystalline surfaces of binary semiconductors. However, only in the recent past a few experimental and theoretical investigations of its vibrational properties have been published. Interestingly, 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. The first experimental studies of the GaAs(110) surface dynamics were done with inelastic He-atom scattering.[1] In particular, two acoustic modes were reported: one with low intensity lying rather flat at 10 meV between $\overline{\Gamma}$ (center of surface Brillouin zone) and $\overline{X}$ (zone boundary along $[\overline{1}10]$), and another comparatively intense mode at 13 meV near $\overline{X}$. These modes are referred to as A_1 and A_2 in the literature. Higher energies are not accessible for He-atom scattering, but have been studied using high-resolution electron-energy-loss spectroscopy (HREELS) with reports of two $\overline{\Gamma}$ modes at energies 17.5 and 23.2 meV.[2] The HREELS work also reports a Fuchs-Kliewer, or surface optical, phonon at 35 meV. Other HREELS experiments detect this phonon at 36.2,[3] 36.0,[4] 35.5,[5] or 36 meV.[6] A very recent HREELS study by Nienhaus and Mönch[7] examines GaAs(110) surface phonons up to 40 meV excitation energy throughout the whole surface Brillouin zone (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.

Apart from these experimental works, a variety of theoretical techniques have been employed to describe the dynamical behavior of the GaAs(110) surface. An interpretation of the A_1 mode as a rotational surface phonon involving the top layer atoms has been suggested by Wang and Duke.[8] The results of their tight-binding (TB) calculation are in good agreement with the experimental findings. Kelin and Zijing[9] claim semiquantitative accordance between the results of their TB approach and experimental findings for A_1 and A_2 modes. However, at the $\overline{\Gamma}$ point they report a pure horizontal polarization of A_1, which should, therefore, not be detectable by means of He scattering. Bond-charge-model calculations[10] report the A_1 mode to be a true surface state near the zone boundary, which develops into a broad resonance at the zone center. Utilizing a TB total-energy model, Godin *et al.*[11] found a surface $\overline{\Gamma}$ phonon at 9.3 meV, which corresponds to a chain-bouncing mode and could, therefore, be detected in He scattering experiments. In 1993, the first *ab initio* calculations of GaAs(110) surface phonons were published. Di Felice and co-workers[12] used a molecular dynamical approach to determine vibrational modes at high-symmetry $\mathbf{k}$ points in the SBZ. In the lower energy range of the spectrum, they predicted the flat A_2 mode at about 13 meV. They also noticed some features with large amplitudes of the atomic displacements at the surface at about 11 meV. These were, however, reported to be mixed with bulk states. Fritsch *et al.*[13] 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 that would explain the A_1 mode found experimentally, but observed a broad feature around 10 meV, arising mainly from a series of states that deeply penetrate into the bulk.

The aim of the present study is to contribute to a better understanding of the surface dynamics of the III-V(110) surfaces. To that end we use an *ab initio* pseudopotential method, which is based on the frozen-phonon approach and, therefore, differs from the ones in Refs. 12 and 13, to calculate the surface phonons modes and frequencies for GaAs(110) at $\overline{\Gamma}$ and $\overline{X}$. The results are discussed in the context of previous theoretical and experimental data. In the $\overline{\Gamma}$ case, the frequencies and eigen-

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vectors are compared with surface phonons calculated for the (110) surfaces of InAs, GaP, and InP, in order to examine the chemical trend.

II. METHOD

Two general *ab initio* approaches for phonon calculations are (i) the frozen-phonon method[14] and (ii) the planar force constant method.[15] These approaches have been described in some detail by Srivastava.[16] In the present work, we have employed the frozen-phonon approach.

Our calculations are based on the application of the density-functional theory within the local-density approximation. We consider an artificially constructed periodic geometry along the surface normal. Its unit cell includes a slab with eight atomic layers of III-V(110) and a vacuum region equivalent in thickness to six atomic layers. The electron-ion interaction is accounted for by using fully separable norm-conserving pseudopotentials.[17] The many-body electron-electron interaction is simulated using the exchange and correlation potential as given by Ceperley and Alder.[18] Single-particle orbitals are expanded into plane waves up to an energy cutoff of 15 Ry. The **k**-space integration is replaced by a sum over four special points in the SBZ. The minimum of the total-energy functional,[19] with respect to both the electronic and atomic degrees of freedom, is found by employing a molecular dynamical approach.[20] Thereby, we determine the surface geometries of the relaxed III-V(110) surfaces in perfect agreement with Ref. 21. Figure 1 illustrates the atomic structure of such a prototypical surface.

The relaxed surface geometries are the starting point for our phonon calculation. In earlier publications,[22] it was shown that the dynamical properties of crystalline surfaces can be reliably described by using a simple restricted dynamical model, using the frozen-phonon approach. 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 atoms of the three outermost surface layers are treated as coupled three-dimensional harmonic oscillators. These atoms are displaced away from their equilibrium positions. The resulting Hellmann-Feynman forces are fitted to a quadratic equation in the distortion and the linear part is extracted. The cubic dependence of the forces on the distortion is found to be negligible. A displacement of 0.1 bohr is chosen. Earlier calculations[22] have shown that the influence of the amplitude of the distortion on the force constants is rather small. The force constants resulting in the harmonic approximation are used to build up the dynamical matrix. Due to the intrinsic symmetry of this matrix, we end up with more force constants than really needed. This redundancy can be conveniently used to fight any round-off errors in the numerical calculation. Once the dynamical matrix **K** is specified, the solution of the eigenvalue matrix equation,

$$\mathbf{M}\ddot{\mathbf{u}} = \mathbf{K}\mathbf{u}, \tag{1}$$

where **M** represents the vector of the atomic masses, yields the surface-atom vibrational normal modes and frequencies. In order to get a feeling for the accuracy of the method employed, we have also calculated the bulk TO(Γ) frequency for the III-V compounds. For GaAs and GaP, the calculated values of $\hbar\omega = 33.9$ meV and 46.1 meV, respectively, are 1.5% and 2.2% larger than the experimental findings.[23] For the more ionic compounds InAs and InP, the deviation between the calculated and measured frequencies is more distinct: our values are larger than experimental results by 7.7 % and 10.0 %, respectively. The theoretical overestimation of the phonon frequency for the indium compounds reflects the corresponding underestimation of the equilibrium lattice constant using the present theoretical method.[21] The level of theoretical accuracy for the bulk phonon result does not imply the same for the surface phonons, since their calculation is more complex. While we expect to get quantitatively reliable results for GaAs and GaP, the results for InAs and InP have to be scaled according to the discrepancies for the bulk TO(Γ) frequencies for such a purpose. Nevertheless, they might at least be useful for discussing qualitative trends.

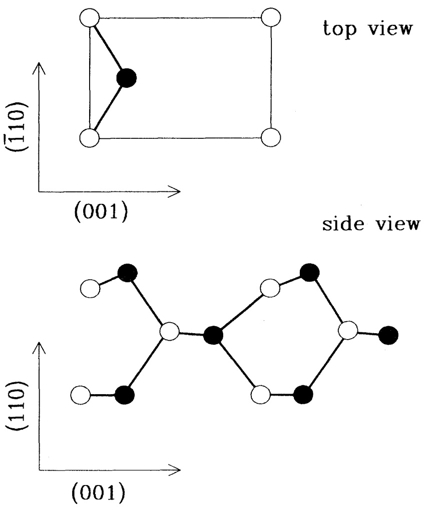

FIG. 1. Side and top view of the relaxed III-V(110) surface. White (black) circles denote the cations (anions).

III. RESULTS

A. GaAs: surface phonons at $\bar{\Gamma}$ and $\bar{X}$

Results of our calculation on GaAs(110) are compiled in Tables I and II. In these tables, a comparison with earlier published results is given. The eigenfrequencies have been ordered according to the displacement pattern they belong to as far as these were given in the references. From the 36×36 eigenvalue problem, we have only selected the modes that describe a more or less pronounced surface character. Our results are set in round brackets when the considered mode does not describe a true surface phonon, but a rather complex displacement pattern with large amplitudes of the outermost surface

TABLE I. Comparison of calculated surface phonon frequencies of GaAs(110) at $\bar{\Gamma}$ with results of earlier calculations and experiments. Frequencies $\hbar\omega$ are given in meV. The results set in parentheses describe a complex dispmacement pattern with large amplitudes of the outermost surface atoms. In square brackets, the change of the macroscopic surface dipole potential (in 0.1 eV) due to the specific distortion pattern of $|u| = 0.1$ bohr is given.

Mode	A'						A''		
Present results [dipole]	(11.1) [0.2]	14.6 [0.3]	(17.7) [0.1]	23.2 [0.1]		35.8 [1.5]	(8.6) [0.0]	31.1 [0.0]	31.7 [0.0]
Ab initio (Ref. 13)		16.2		23.7	30.9	34.6		30.0	32.2
Ab initio (Ref. 12)	11.0	13.3			27.3	34.1			
Bond charge (Ref. 10)	9.6								
Tight binding (Ref. 9)							9.8		
Tight binding (Ref. 8)	10.7								
He scattering (Ref. 1)	10.0								
HREELS (Ref. 2)			17.5	23.2		35.0			
HREELS (Ref. 7)	10.5		16.5	21.1		35.8			

atoms.

The surface phonons at the center of the SBZ, $\bar{\Gamma}$, can be classified according to the irreducible representations of C_S (or m), the point group symmetry of the surface unit cell. Thereby, A'' modes describe lattice distortions along the $[\bar{1}10]$ direction, i.e., along the III-V zigzag chains, whereas A' modes correspond to atomic displacements perpendicular to the chain direction. In contrast to the $\bar{\Gamma}$ case (Table I), such a clear classification of modes is not possible 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. In general, modes at $\bar{X}$ represent mixtures of a shear-horizontal and a sagittal-plane polarization, i.e., the atomic displacements have nonzero components in all Cartesian directions. In Table II we have given the sum of the square of the sagittal and the shear-horizontal vector components for all eigenmodes at $\bar{X}$.

From Tables I and II, it is obvious that not all modes expected from theoretical point of view have been detected experimentally. This is not so surprising. One reason could be low scattering efficiency for some modes. In particular, the A'' modes at the $\bar{\Gamma}$ point 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 some surface modes. Within the slab approach and restriction to a few atomic layers which are allowed to vibrate, the number of surface phonons is not well defined. Moreover, only the Fuchs-Kliewer phonon frequency lies above the highest bulk phonon frequency, all other surface phonon frequencies lie in the range of bulk phonon band structure of GaAs.

The two lowest energies shown in Table II correspond to surface acoustic displacement patterns. They are energetically very close (with an energy difference of only 0.2 meV) and, therefore, probably cannot be resolved in the scattering experiments. We find their energetical po-

TABLE II. Comparison of calculated surface phonon frequencies $\hbar\omega$ (in meV) of GaAs(110) at $\bar{X}$ with results of earlier calculations and experiments. As in Table I, the results shown in parentheses describe a complex displacement pattern with large amplitudes of the outermost surface atoms. In square brackets, we give the sum of the square of the sagittal (SG) and the shear-horizontal (SH) vector components.

Mode	Rayleigh		Other acoustic and optical modes							
Present results $[\sum u_{\mathrm{SG}}^2]$ $[\sum u_{\mathrm{SH}}^2]$	8.7 [0.68] [0.32]	8.9 [0.70] [0.30]	(11.1) [0.51] [0.49]	13.0 [0.50] [0.50]	14.2 [0.51] [0.49]	22.7 [0.93] [0.07]		28.2 [0.79] [0.21]	32.0 [0.89] [0.11]	35.5 [0.42] [0.58]
Ab initio (Ref. 13)	8.6	8.9		13.0	14.5			27.4		34.4
Ab initio (Ref. 12)	4.4	8.8	11.0		13.6	22.3	22.9		30.0	33.5
Bond charge (Ref. 10)	7.6	8.2	9.5	13.3						
Tight binding (Ref. 9)	6.4	7.7	12.4	13.6						
Tight binding (Ref. 8)			12.6							
He scattering (Ref. 1)	8.3		10.0	13.0						
HREELS (Ref. 7)	8.6				14.8	21.5				36.2

sitions in close agreement with Ref. 13, but at variance with other theoretical results,[9,10,12] which report a larger splitting between the two frequencies. In agreement with the result by Fritsch *et al.*,[13] 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 has a complementary character, which is also reported in Refs. 12 and 13. Both phonons have displacement vectors, which are partly in the sagittal plane and can, therefore, be understood as Rayleigh waves although there is considerable confusion in the literature concerning their notation. The acoustic eigenmodes at $\overline{X}$, predicted in earlier model calculations,[9,10] differ from our findings.

Experimentally, a surface phonon branch at about 10 meV (denoted as A_1 in the literature) has been found.[1,7] At the $\overline{\Gamma}$ point, this surface phonon should have A' symmetry. Therefore, the A_1 mode discussed in Ref. 9 should not correspond to the experimental findings, but rather to the lowest A'' frequency found in our calculation. We find at 11.1 meV an A' phonon, which is best described as a rotational mode of the GaAs chain on the surface. Although there is an appreciable contribution of the outermost surface atoms, we still observe considerable displacements of the atoms in the deeper layers and would, therefore, not classify this mode as a surface phonon. However, our result is in surprisingly good agreement with an earlier work by Wang and Duke,[8] who predicted a frequency of 10.7 meV corresponding to the rotation of the top layer GaAs chain. Rather similiar is the 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. Both describe chain-bouncing modes in which the orientation of the surface zigzag chain, with respect to the underlying substrate, changes as the surface atoms move strongly in the [110] direction. They show 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, in agreement with earlier calculations which determine its energy either at 13.3 (Ref. 12) or 16.2 meV. (Ref. 13) He scattering experiments resolved a surface phonon at $\overline{X}$ at 13.0 meV (denoted A_2 in the literature). We find in nearly perfect agreement with Refs. 10 and 13 a vibrational state dominated by the displacement of the first layer Ga ions in the chain direction and of the uppermost As ions perpendicular to the surface chains.

At a somewhat higher energy of 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 surface normal. However, second and third layer cations also contribute to that mode. In this energy range, the HREELS experiments[2,7] measured an energy loss. However, both experimental groups reported this loss to be weak. At the zone boundary ($\overline{X}$), we find at 14.2 meV a surface phonon, which is strongly localized at the outermost cation in accordance with the calculation by Fritsch *et al.*[13] The first layer Ga atoms vibrate perpendicular to the plane defined by the first- and second-layer As atoms. Di Felice *et al.*[12] found a similiar displacement pattern for this mode, but with a slightly lower energy.

Also detected experimentally[2,7] is a surface phonon 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, in agreement with other results.[12]

The highest phonon energy detected experimentally is the Fuchs-Kliewer mode between 35 and 36 meV. In close agreement to Refs. 13 and 24 the calculated corresponding displacement pattern shows mainly a bond stretching character between first layer cation and second-layer anion. In Table I, we have also presented the change in the macroscopic dipole potential of the GaAs(110) surface caused by the specific displacement pattern in the $\overline{\Gamma}$ case. As expected, the A'' modes do not give rise to any change of the surface dipole. 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. Consequently, we conclude that the excitation of this mode is related to the macroscopic electric field. This mode actually corresponds to the Fuchs-Kliewer phonon detected in a number of HREELS experiments, as discussed in the introduction. Figure 2 illustrates the atomic displacement associated with this phonon. The net dipole with a strong normal component after excitation of the Fuchs-Kliewer phonon can be seen. The small dipole changes for the other A' modes may be related to piezoelectricity.

Altogether we find that all the surface phonons observed experimentally are rather reliably reproduced in our calculation. Possibly by means of more polarization-sensitive techniques, such as Raman scattering,[25] other phonons such as the A'' modes at $\overline{\Gamma}$ can be resolved. Also, the agreement with another *ab initio* calculation[13] is rather complete. The existing differences between our results and those of Fritsch *et al.* are most likely to be due to slightly different approaches used: e.g., frozen-phonon calculation instead of planar force constant method, dif-

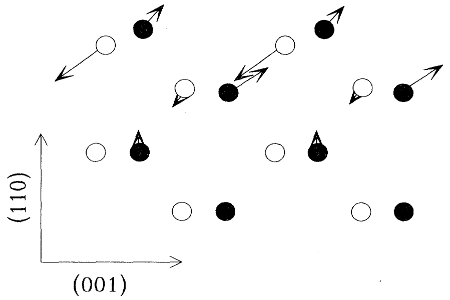

FIG. 2. Displacement pattern of the surface $\overline{\Gamma}$ optical phonon of GaAs(110) at 35.5 meV with A' symmetry. White (black) circles denote the cations (anions).

TABLE III. Comparison of calculated surface phonon frequencies $\hbar\omega$ (in meV) on III-V(110) surfaces at $\bar{\Gamma}$ with results of an earlier calculation and experimental data. As in Tables I and II, the results shown in parentheses describe a complex displacement patter with large amplitudes of the outermost surface atoms.

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. 8	7.7											
Ref. 27							29					
GaAs	(11.1)	14.6	(17.7)	23.2			35.8	(8.6)			31.1	31.7
Refs. 2–6							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. 8	7.8											
Ref. 4							41.8					
Ref. 28							42.0					
Ref. 29	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. 8	12.0											
Ref. 4							49.1					
Ref. 30							48.0					

ferent pseudopotentials as well as different energy cutoffs. The reported deviations from the results by Di Felice *et al.*[12] are more serious and could be due to the relatively small number of atomic layers used in their calculation.

B. InAs, GaAs, InP, and GaP: chemical trend

In order to deduce a chemical trend for the dynamical properties of III-V(110) surfaces, we have also performed calculations of the surface $\bar{\Gamma}$ phonons of InAs, GaP, and InP. The results are summarized in Table III. The eigenfrequencies are ordered according to the symmetry of the displacement patterns. The results are set in parentheses when they do not describe a clearcut surface phonon, but a distortion pattern with large amplitudes of the outermost surface atoms.

The force constant matrices of the four systems are rather similiar and, therefore, of minor influence in governing a chemical trend. To illustrate this, we diagonalize Eq. (1) with the mass vector $\mathbf{M}$ of GaAs for all the four systems. We obtain rather similiar eigenmodes and the corresponding eigenvalues scatter within a range of only 3 meV. In particular, we obtain the following frequencies for the Fuchs-Kliewer phonon: 38.1 meV (GaP), 37.5 meV (InP), 35.8 meV (GaAs), and 35.2 meV (InAs). The resulting variation of these eigenvalues can be traced back to the different bonding properties. One characteristic parameter is the heat of formation: it decreases as $\Delta H_f(\mathrm{GaP}) > \Delta H_f(\mathrm{InP}) > \Delta H_f(\mathrm{GaAs}) > \Delta H_f(\mathrm{InAs})$ (see, e.g., Ref. 23). A clear correlation of the chemical trend with the polarity of the chemical bond or the Born dynamical charge[23] does not exist.

The most important chemical trend for the phonon frequency and atomic displacement pattern on III-V(110) is provided by the constituent masses. A good example for such a trend is provided by the study of the Fuchs-Kliewer phonon. As shown in Fig. 2 for GaAs(110), the eigenmode of this phonon essentially describes a bond stretching between first-layer cations and second-layer anions. The character of this mode remains the same for the other considered surfaces. Only the magnitudes of the displacements vary. Thereby the relative amplitudes of the cation and anion motion in the top two surface layers are roughly given by their inverse mass ratio. In Fig. 3, the frequency variation of this phonon is plotted against the square root of the inverse reduced mass of the surface cation and anion. We nearly observe a linear behavior. This trend is similar to that known for the bulk TO(Γ) frequencies. However, we find that the difference between the bulk TO(Γ) frequency and the Fuchs-Kliewer phonon frequency increases with lighter reduced mass.

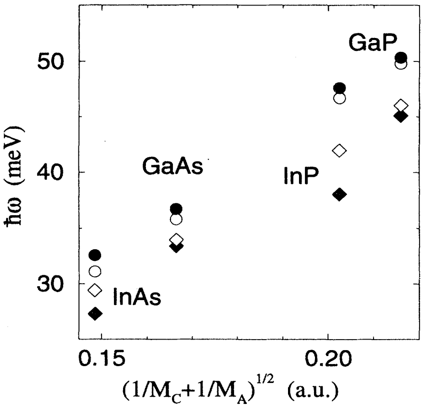

FIG. 3. The measured (Ref. 23) bulk TO(Γ) frequencies (black diamonds) are compared with the calculated values (white diamonds). From the latter we estimate, according to Eq. (2), the frequencies of the Fuchs-Kliewer phonons (black circles). These values are compared with our full calculation of the Fuchs-Kliewer frequencies (white circles).

The Fuchs-Kliewer phonon frequency is related to the bulk TO(Γ) frequency by[26]

$$\omega_{\text{FK}} = \omega_{\text{TO}} \sqrt{\frac{\epsilon_0 + 1}{\epsilon_\infty + 1}}, \tag{2}$$

where ϵ_0 and ϵ_∞ are the static and the optical dielectric constants, respectively. The frequency of the Fuchs-Kliewer phonon can be estimated according to Eq. (2) from that of the bulk TO(Γ) as shown in Fig. 3. The influence of the dielectric properties is rather well described since the microscopic electric fields are fully acounted for in our total-energy calculations. However, since the TO(Γ) frequency for the Indium compounds is somewhat overestimated in our calculations, we find a similar overestimation for the energy of the surface optical phonon in case of InAs and InP. This becomes obvious from a comparison with experimental data. For InAs(110) the surface optical phonon has been found at 29 meV,[27] whereas for InP(110) the values 41.8,[4] 42.0 meV,[28] and 42.5 meV (Ref. 29) have been reported. Comparing our data to these experimental values, we find an overestimation of the Fuchs-Kliewer phonon energy by about 4 (InP) and 2 meV (InAs). It scales with the magnitude of the overestimated bulk TO(Γ) frequency discussed above. The agreement between calculated and measured frequencies is much better in the case of GaP(110). Here, the experimental findings for the Fuchs-Kliewer frequency of 49.1 (Ref. 4) and 48.0 meV (Ref. 30) are only slightly smaller than our result of 49.8 meV.

A similiar trend with the masses can be found for the highest energy A'' phonons. For all the compounds considered here, these modes are dominated by a horizontal shear motion of the uppermost III-V chain along $[\bar{1}10]$. Their frequencies steadily increase if one goes to compounds with lighter reduced mass. The magnitude of the displacement of the individual atoms is also correlated to the inverse atomic masses. Furthermore, 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 under consideration 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 case of GaAs. Consequently, for instance, the A' modes of InP at 34.2 and 36.0 meV are more strongly localized at the surface than the 23.2 meV mode for GaAs. They really 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. Nevertheless, as can be seen from Table III, most eigenmodes can be classified according to the displacements discussed in detail in the case of GaAs(110). Thus, 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. 4. There the frequencies of Table III are plotted either against the square root of the cation mass (for acoustic modes) or against 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 behavior indicating only negligible fluctuations of the force constants for the four III-V(110) surfaces.

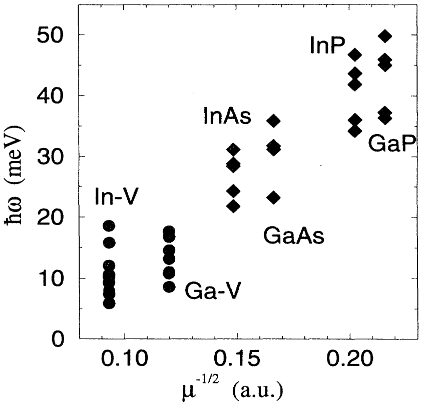

FIG. 4. Calculated frequencies of surface phonons (given in Table III) are plotted against the square root of the inverse mass. For optical modes (black diamonds), the reduced masses are taken, whereas for acoustic modes (black circles) the square root of the respective inverse cation mass is considered.

IV. SUMMARY

We have performed *first principles* calculations for the dynamical properties of the (110) surface of GaAs, InAs, GaP, and InP, in the framework of the frozen-phonon approach. The calculated vibrational eigenmodes for GaAs(110) at $\bar{\Gamma}$ and $\bar{X}$ are in good agreement with the existing experimental and theoretical results. The controversially discussed A_1 mode can be described as a rotational phonon of the surface GaAs chains (the lowest frequency A' phonon in this work). However, the localization of this mode at the surface is, to our mind, too weak to 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 with Fuchs-Kliewer phonon, which is found in several HREELS studies.

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 structure play only a minor role for the localization properties of surface phonons.

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