PHYSICAL REVIEW B VOLUME 41, NUMBER 8 15 MARCH 1990-I

Dispersion relations of low-energy branches in the vibrational spectrum of cleaved GaAs(110)

Wang Kelin and Lin Zijing*
Center for Fundamental Physics, University of Science and Technology of China, Hefei 230026, Anhui, People's Republic of China

(Received 23 March 1989; revised manuscript received 16 October 1989)

A realistic calculation of the low-frequency phonon spectrum of cleaved GaAs(110) is presented. Our calculation is based on Chadi's tight-binding theory for structural energies and the structural energies are simply determined by the bond-orbital approximation. A variety of interesting surface vibrational modes are found which agree well with the observation, in He-atom scattering experiments, of some acoustic branches of surface phonons.

Cleaved GaAs(110) surfaces undergo a well-documented (1×1) reconstruction in which the surface relaxes by a 30° bond length, conserving rotation in a plane normal to the surface along the zig-zag chains of alternating As and Ga atoms with the As atoms rotating outward and the Ga atoms rotating inward to the surface.[1,2] This reconstruction should be reflected in the surface lattice dynamics, although it is not clear *a priori* just what the effects should be. Recently, surface-phonon dispersion curves for this surface have been measured by Harten and Toennies (HT) (Ref. 3) and Doak and Nguyen (DN).[4] Here we will present preliminary results of a theoretical calculation of the low-energy phonon spectrum of the surface. A comparison of our calculation with experimental results is also provided.

Our lattice-dynamics calculations are based on Chadi's tight-binding theory for the valence electronic structural energies in semiconductors.[5] Models of this type have been used to calculate geometries and vibrational excitations of reconstructed surfaces.[5-8] In the model, the total energy of the system is partitioned into two pieces:

$$E_{\text{total}}=E_{\text{band}}+E_{\text{elastic}} . \tag{1}$$

Here E_{band} is the sum of independent particle energies from the filled valence bands.

A tight-binding description of the valence electronic structure which includes all five independent nearest-neighbor hopping amplitudes among a set of four tight-binding valence orbitals per atomic site is adopted to calculate these bands. The relevant hopping amplitudes are chosen to reproduce the valence electronic structure and assumed to scale as $1/d^2$ with interatomic distance in different structures. The bond-orbital approximation[9] which is reasonable for nonmetallic surfaces is used here to further simplify the calculation of the energies of these valence bands.

The second term in Eq. (1) is an effective short-range elastic energy which is written as a sum on bonds i:

$$E_{\text{elastic}}=\sum_i (U_1x_i+U_2x_i^2) , \tag{2}$$

where $x_i=d_i/d_0-1$ is the fractional deviation of the bond length d_i from its equilibrium value d_0 in crystalline GaAs. The elastic parameters U_1 and U_2 are fitted to properties of GaAs in zinc-blende crystal structure. It has been shown that an overall reasonable agreement between theoretical and experimental bulk-phonon dispersion curves can be obtained by choosing suitable value of U_1 and U_2. For GaAs bulk-phonon dispersion relations, the poorest comparison occurs at TA(X) where the vibrational frequency is overestimated by 12%. This feature approves the effectiveness of the method in studying phonon spectra.[8]

Using the model described above, some analytical expressions for force-constant calculation which take into account the relaxation of surface atoms and the rehybridization of the valence states can be derived. These expressions for force-constant calculation have been applied to study vibrational excitations of several semiconductor surfaces and shown to be simple and effective.[8] As GaAs is a polar material, there exists additional long-range Coulomb interaction for longitudinal-optical phonons. This interaction causes the splitting of LO and TO mode of bulk vibration and induces a Fuchs-Kliewer surface optical phonon.[10] Nevertheless, such kind of interaction results in much complexity in realistic surface-phonon calculations. Fortunately, the frequency of this polar optical surface-phonon mode is determined by the macroscopic dielectric constant $\epsilon(\omega)$ of the material and contains no information on the microscopic properties of the surface. From this point of view, we neglect the long-range Coulomb interaction and direct our attention to the acoustic branches that are not related to the polar Coulomb interaction, in the surface vibrational spectrum.

Using a fifteen-layer slab, the surface-vibrational spectrum for low-energy branches is shown in Fig. 1. The solid curve within Fig. 1 is the lowest edge of the projected bulk vibrations in our calculation. The dashed lines represent dispersion relations of the surface phonons on GaAs(110). The modes labeled as R_1 and R_2 are outside of the bulk bands and must therefore be surface modes, i.e., Rayleigh modes. The polarizations of R_1 and R_2 in the surface layer are as follows: R_2 is primarily a longitudinal mode, i.e., it is primarily associated with vibra-

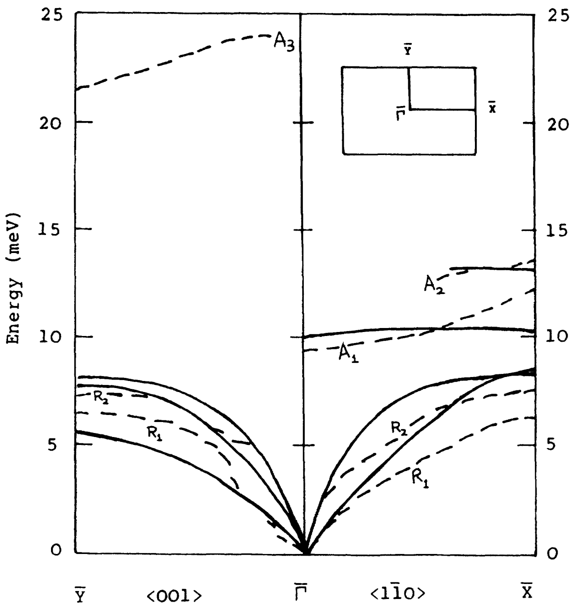

FIG. 1. Theoretical (dashed lines) and experimental (solid lines) results for surface-phonon dispersion curves in the acoustic region of the spectrum. The surface Brillouin zone is shown in the inset.

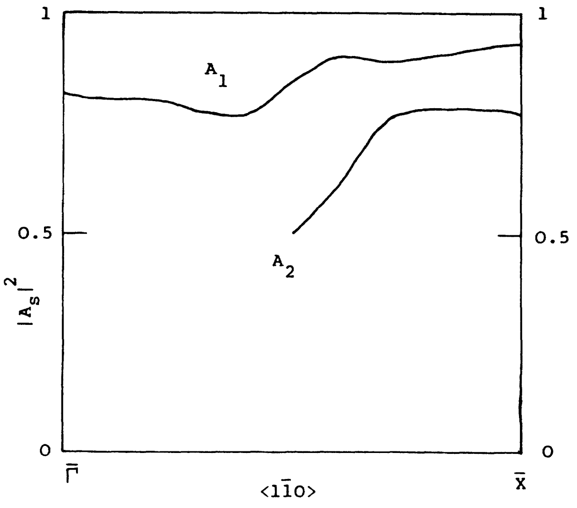

FIG. 2. The sum of the squared amplitudes of two inequivalent atoms in surface layer, $|A_s|^2$, as a function of the wave vectors for surface modes A_1 and A_2.

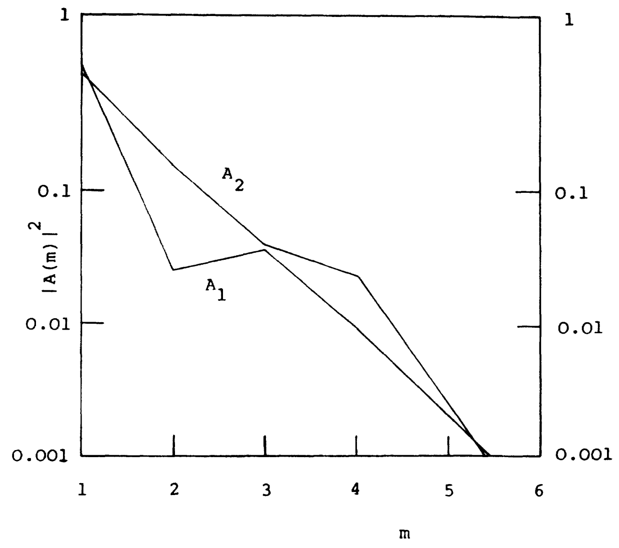

FIG. 3. The sum of the squared amplitudes of two inequivalent atoms in each layer for surface modes A_1 and A_2 which lie at the $\bar{x}$ point, $|A(m)|^2$, vs layer index m, with $m=1$ for the surface layer.

tions in the direction parallel to its wave vector $\bar{q}$; R_1 is primarily a transverse mode and polarizes mainly in the $\langle 001\rangle$ direction for $\bar{q}$ in the $\langle 1\bar{1}0\rangle$ line and is primarily associated with vibrations normal to the surface for $\bar{q}$ in the $\langle 001\rangle$ direction. Both modes, however, are not pure longitudinal or transverse. Modes A_1 and A_2 are to some extent mixed with bulk phonons. At the $\bar{\Gamma}$ point, A_1 is purely polarized in the direction parallel to the zig-zag chain ($\langle 1\bar{1}0\rangle$ direction). With the increasing difference of the wave vector from the $\bar{\Gamma}$ point along the $\langle 1\bar{1}0\rangle$ direction, the vibration of A_1 has a larger and larger component perpendicular to the zig-zag chain, though the vibrations along the zig-zag chain remains the dominant. The A_2 mode is mainly polarized in the plane perpendicular to the zig-zag chain with a small component along the zig-zag direction. The two modes indeed belong to the surface, and are shown by the fact that their calculated eigenvectors are larger near the surface and decrease rapidly with increasing distance from the surface. In Fig. 2, the sum of the squared amplitudes of two unequal atoms in surface layer (normalized as one for the whole slab), is plotted as a function of the wave vectors for A_1 and A_2, respectively. It can be easily found that A_1 is more localized in the surface layer than A_2. To show the vibrational distribution of surface modes A_1 and A_2, the sum of the squared amplitudes, which correspond to a wave vector of surface Brillouin-zone boundary $\bar{X}$, of two unequal atoms in each layer is plotted as a function of the layer index m, with $m=1$ for the surface layer in Fig. 3. In the $\langle 001\rangle$ direction, it is difficult to find some clear surface modes like A_1 and A_2 from the distribution of atomic vibrations. HT and DN have measured surface-phonon dispersion curves along the $\langle 1\bar{1}0\rangle$, $\langle 1\bar{1}1\rangle$, $\langle 001\rangle$, and $\langle 1\bar{1}2\rangle$ azimuth of GaAs(110) by using He-atom inelastic scattering. For a comparison, some typical results of the experiments are given in Fig. 1. Besides a Rayleigh mode, HT's experiment shows there are two surfaces modes A_1 and A_2 along the $\langle 1\bar{1}0\rangle$ azimuth. A_1 is a mode with a nearly wave-vector-independent energy of 10 meV, and A_2 appears only in the vicinity of the Brillouin-zone boundary with an energy roughly 13 meV. The predicted energy values of our calculation are semiquantitatively in accord with the experimental results. With energies similar to experimental values, the theoretical dispersions of A_1

and A_2 are quite weak, though not so weak as measured. From the Brillouin-zone center to its boundary, the calculated energy of A_1 arises from 9.8 to 12.4 meV. The energetical range of A_2 is 12.6–13.6 meV.

Only one Rayleigh mode is found along the $\langle 1\bar{1}0 \rangle$ direction instead of two predicted by calculation. The reason for this discrepancy between theory and experiment is that the scattering in the azimuth might not be particularly sensitive to the motion of the displaced Ga atoms, whose oscillations in and out of the tetragonal pockets would project primarily along the $\langle 001 \rangle$ azimuth. Indeed, both R_1 and R_2 are found in the direction of $\langle 001 \rangle$ by Doak and Nguyen and qualitatively agree with our calculation. Nevertheless, the quantitative differences between theory and experiment are notable. Taking the accuracy of the method into consideration, however, the comparison of our calculated surface-phonon dispersion to the experimental results of HT and DN is satisfactory. Because of the bond-length conserving character of the structure of the cleaved GaAs(110), the elastic energy as shown in Eq. (2) and its contribution to surface force constants change little from the bulk to the surface. The above discrepancy between calculation and experiment should be mainly related to the electronic band energy which is calculated here by the bond-orbital approximation where the detailed band structures are difficult to be seen. Using a more precise calculation method and taking the details of the surface band structures into account, one can expect that the agreement between theory and experiment will be better and the microscopic mechanism of the surface lattice dynamics will be revealed more clearly.[7] As the structure of cleaved GaAs(110) is well established, this agreement shows that the lattice-dynamical method we used is reliable. Moreover, this fact means that it is not necessary to introduce such types of forces between the surface atoms that are distributed to make some localized vibrations of atoms or groups can take place in order to explain the experimental behavior of A_1 as suggested by HT.[3] In fact, such localized vibrations are not allowed in the presently accepted geometry of GaAs(110).

It may be worthy to mention that, apart from the above four surface modes, our calculation gives an additional surface mode A_3 along the $\langle 001 \rangle$ that is not found in DN's experiment. As the energy of A_3 may be too high to be distinguished by present He scattering, a more effective experimental approach with higher accuracy will be helpful to provide a more complete knowledge of phonons on this surface and verify the existing surface-dynamics theory in a more complete way.

In summary, we have obtained the low-frequency phonon spectrum of the cleaved GaAs(110) surface and found that our calculated phonon spectrum is in qualitative agreement with the observations of He-atom scattering experiments.

---

[*] Present address: Theoretical Group, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, China.

[1] C. B. Duke and A. Paton, Surf. Sci. **164**, L797 (1984).

[2] S. B. Zhang and M. L. Cohen, Surf. Sci. **172**, 754 (1986).

[3] U. Harton and J. P. Toennies, Europhys. Lett. **4**, 833 (1987).

[4] R. B. Doak and D. B. Nguyen, J. Electron. Spectrosc. Relat. Phenom. **44**, 205 (1987).

[5] D. J. Chaid, Phys. Rev. Lett. **41**, 1062 (1978); **43**, 43 (1979).

[6] D. C. Allan and E. J. Mele, Phys. Rev. Lett. **53**, 826 (1984).

[7] O. L. Alerhand and E. J. Mele, Phys. Rev. Lett. **59**, 657 (1987); Phys. Rev. B **35**, 5533 (1987).

[8] Z. J. Lin and K. L. Wang, Phys. Status Solidi B **148**, 525 (1988); **149**, 143 (1988); Acta Phys. Sin. **37**, 1932 (1988).

[9] W. Harrison, *Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980).

[10] R. Fuchs and K. L. Kliewer, Phys. Rev. **140**, A2076 (1965).