Phonon spectra of (001), (011) and (111) surfaces and interfaces of the CdTe/HgTe system

Phonon spectra of (001), (011) and (111) surfaces and interfaces of the CdTe/HgTe system

R Rey-Gonzalez, L Quiroga and A Camacho

Departamento de Física, Universidad de los Andes, AA 4976, Bogota DC, Colombia

Abstract. Phonon spectra of CdTe and HgTe surfaces and interfaces are calculated within a Green function formalism. The dependence of phonon density of states spectra on the surface orientation is studied. Of the two compounds considered, HgTe shows the most drastic modification of its phonon structure as a surface is created. (001) and (111) polar interfaces show very different vibrational properties: while the former exhibits a two-mode or persistent behaviour with a vanishing phonon gap for any polarization, the latter exhibits a one-mode behaviour depending on the vibration polarization. For the (011) interface a two-mode behaviour is obtained, where bulk optical modes of one compound penetrate some distance into the other compound. The obtained phonon spectra show interface induced effects in a frequency range where Raman scattering data in CdTe/HgTe superlattices were previously reported but not explained.

1. Introduction

The CdTe/HgTe system has attracted much attention because of interest in the technological capabilities of the alloy as well as of quantum wells and superlattices built up from these materials. For example, CdTe/HgTe heterostructures are considered to be a prime candidate for infrared optoelectronic devices [1–3]. Due to the high ionicity of these compound semiconductors carrier mobility as well as optical response in CdTe/HgTe based devices must be limited mainly by electron–phonon scattering from longitudinal optic phonons. Although technological development of these systems seems to have been hampered considerably by disturbing effects such as cation diffusion at the interfaces, their vibrational properties still lack a precise description. The phonon spectra of CdTe/HgTe surfaces and single interfaces have just started to be considered [4, 5], in spite of the paramount importance of phonons to obtain a reliable theoretical description of the main optical and transport properties of heterojunctions based on this system.

CdTe/HgTe superlattices have been Raman analysed, showing confined optical phonons in the HgTe and CdTe layers as well as phonons from alloy layers formed at the interfaces [6, 7]. Besides that, another distinct peak also appears in the experimental data at a frequency in between those of the optical phonons of each perfect crystal [7]. In spite of no definitive explanation being furnished of its origin, the possibility of linking this feature with an interface induced phonon mode is still open. Although the folding of acoustic branches and the confinement of the optical modes are essentially originated by the superlattice geometry and by the spectral features of the composing materials, the most interesting dynamical properties of this system are expected to be due to the perturbation induced by the physical interface. One of the aims of this paper is to provide clues to understanding the origin of

interface active modes in Raman spectra of this system, by studying, besides the surface vibrational properties, the phonon spectra of single interfaces.

Bulk phonons of some II–VI semiconductors have been considered recently, from a theoretical point of view, by *ab initio* calculations by Dal Corso *et al* [8]. *Ab initio* calculations are the most appropriate answer to this problem but it is far from realistic now to apply them to heterostructures. Therefore, yet another method of calculation, which allows an easy and quick test of models, hypothesis and geometrical situations, has proven desirable. In this paper we illustrate the use of a very simple method that takes full advantage of the existing ingredients for the calculation of phonon spectra for surfaces and interfaces of semiconductors. Besides that, the model we employ offers a realistic calculation scheme going beyond simple analysis such as linear chain models (limited to analysing phonon modes with wavevectors perpendicular to the interfaces), and, on the other hand, allows us to gain information from a microscopic point of view (in contrast to a macroscopic dielectric continuum approach) as it works with a three-dimensional discrete crystal description. We use a force constant model, in which the polarization in an ionic crystal is determined completely by the displacement of ions (assumed to be point like) from their equilibrium positions. The polarization within the ions is ignored.

In order to obtain a clear physical picture for differently oriented surfaces and interfaces, and therefore to provide guidelines to interpret infrared and Raman data, we present in this paper the first systematic investigations on the surface/interface orientation dependence of phonon spectra for CdTe/HgTe surfaces and interfaces grown in the (001), (011) and (111) directions. Each of these compounds is a zincblende crystal with roughly the same lattice constant, so strain effects in the interface case are negligible. Atomic planes perpendicular to the (001) and (111) directions are formed by a single kind of atom: it is therefore necessary for these directions to distinguish between anion and cation layers. They are called polar planes. Atomic planes perpendicular to the (011) direction are formed by an equal number of anions and cations. They are, therefore, non-polar planes. In order to elucidate the vibrational properties of these systems, we employ a Green function (GF) formalism, together with a transfer matrix approach, to obtain the phonon density of states (PDS). This method of calculation provides an exact solution to the surface and interface GFs, since it takes into account the true semi-infinite media forming the crystal with a free surface or the bicrystal in the interface case, avoiding the undesirable slab effects.

In the following section, we present the theoretical model used to calculate the phonon spectra. In section 3, we present and discuss the results of our calculations for both surfaces and interfaces. Our conclusions are given in section 4.

2. The theoretical approach

Since two-dimensional periodicity is retained in the surface and interface systems we are interested in, and $k_\parallel$ is a good quantum number, the system will be described in terms of principal layers. A principal layer is defined so that it interacts only with its nearest-neighbour principal layers, and this accounts for all interactions in the crystal. With the present model one principal layer contains two atomic planes. In order to obtain the phonon spectra we start with the equation of motion in the framework of the harmonic approximation:

$$(\mathcal{M}d^2/dt^2 + \phi)|u\rangle = 0 \qquad (1)$$

where $\mathcal{M}$ and ϕ are the mass matrix and the force constant matrix respectively. In (1) $\langle n, l, b, j | u \rangle$ is the displacement along the j direction ($j = x$, y or z) of the bth atom in a unit cell at the site n within a given atomic plane in the lth principal layer. $b = a$ or c stands for anions or cations, respectively.

We search for solutions to (1) of the form

$$\langle n, l, b, j | u \rangle = M_b^{-1/2} \langle k, l, b, j | u \rangle \exp(i k \cdot n - \omega t) \tag{2}$$

where ω is the frequency of a normal mode. In analogy with the electronic problem we call these solutions of the Bloch–Wannier form. This basis set reflects the symmetry of each semi-infinite crystal and is therefore well suited for our purpose. The secular equation we obtain is given by

$$(\omega^2 \mathcal{I} - \mathcal{D}) | u \rangle = 0 \tag{3}$$

where $\mathcal{I}$ is the unit matrix appropriate for the surface or interface system and $\mathcal{D}$ is the dynamical matrix with elements, in the mixed Bloch–Wannier basis, given by

$$\langle k, l, b, j | \mathcal{D} | k, l', b', j' \rangle = (M_b M_{b'})^{-1/2} \sum_n \langle 0, l, b, j | \phi | n, l', b', j' \rangle \exp(i k \cdot n). \tag{4}$$

The problem is thus reduced to finding an appropriate model for the dynamical matrix. It is worth noting that the diagonal elements of the dynamical matrix contain the so called on site terms of the force constant matrix, which are obtained by satisfying a well known sum rule [9]. This must be remembered when a surface or an interface is created, so the corresponding force constants must be cancelled or replaced by different values. The spectral distribution of phonons for the surface and interface systems is then obtained by solving for the system's GF

$$(\omega^2 \mathcal{I} - \mathcal{D}) \mathcal{G}(\omega^2 + i\varepsilon) = 0 \tag{5}$$

where a small imaginary part ε is added to the frequency variable to guarantee a proper definition of the GF on the real axis. In all the calculations we report below ε is taken as half the step in the squared frequency mesh. The value of ε was found convenient in practice. A larger value would reduce computer time considerably but with too much loss of accuracy with the same frequency mesh. The solution for the GF is obtained by decimation, using a quickly converging transfer matrix algorithm [10–12], which provides an exact solution of the GF, allowing surface and interface phonons to be unambiguously determined and to obtain the local PDS at any desired layer for each semicrystal. The local PDS associated with vibrations along the j direction, of a b type atomic plane in the lth principal layer, is given by

$$\rho_{b,j}(\omega, k, l) = -(2\omega/\pi) \mathrm{Im}[\langle k, l, b, j | \mathcal{G}(\omega^2 + i\varepsilon) | k, l, b, j \rangle] \tag{6}$$

where Im denotes the imaginary part. By appropriately choosing the vibration directions j as contained within and perpendicular to the atomic planes forming the surface or the interface, we can easily separate the polarization contribution to the PDS. The k integrated layer PDSs have been obtained by a weighted sum in the Cunningham special points of the two-dimensional Brillouin zone [13].

Shell models are the usual standards for lattice dynamics calculations of zincblende semiconductors, CdTe included [14]. In order to keep the computations as simple as possible

while capturing the main physics of the vibrational structure of the layered CdTe/HgTe system, we employ a force constant model without Coulomb terms. It should be pointed out that the features our force constant model neglects have only a minor influence on the properties investigated here, i.e. integrated layer density of phonon modes, given that their main effect is at and around the Γ point, which contributes little to the total density because of the relatively small volume in reciprocal space. On the other hand, the effects of the long-range Coulomb forces are significant only in the long-wavelength limit and the direct effect on the global features of the density of phonon states can be considered to be fairly small [15]. Besides that, although the Coulomb interaction is indeed long ranged, it is known that the interplanar Coulomb force constants derived from the Coulomb coefficients are in fact rather short ranged. Therefore, here we consider an eight-parameter phenomenological force constant model with first- and second-nearest-neighbour force constants for describing the lattice dynamics of CdTe and HgTe. While explicitly ignoring the long-range Coulomb forces, we note that a model with first- and second-nearest-neighbour empirically fitted force constants can at least adequately represent the effects of the long-range Coulomb forces at the zone boundary points (which dominate the PDS spectrum). The parameter set chosen corresponds to that given in [16], which has proven to provide a good description of the Raman spectrum of HgCdTe alloys. The interfacial force constants are taken to be equal to the geometric mean of the force constants for the materials that form the interface. The sign of the greatest one, when the two force constants have different sign, and the common sign, when they have the same sign, was chosen. It is expected that the interface results are more sensitive to the force constant signs than to its absolute value.

We shall consider ideal (no reconstruction, no relaxation, no disorder) free surfaces, perpendicular to the (001), (011) and (111) directions. For these same directions ideal lattice matched interfaces are studied. Surface relaxation and consequent changes of the force constants at and close to the surface or interface are a problem. In order to address this problem the interaction potentials have to be known. In the case of CdTe and HgTe this is a major problem. A proper solution would be to base the whole treatment on an *ab initio* basis in starting from the electronic ground state energy as a function of the ion coordinates. This is hardly feasible and beyond the scope of the present work.

3. Results and discussion

3.1. Surfaces

We study the dependence of PDS spectra on the surface orientation. In figures 1–3 we display the calculated PDS for (001), (111) and (011) surfaces, respectively. In order to observe easily surface induced effects, PDSs of both surface and bulk atomic planes are shown simultaneously. Because of the large difference of masses between light cadmium atoms (186×10^{-27} kg) and heavy mercury atoms (333×10^{-27} kg) a very different behaviour of CdTe and HgTe anion terminated surfaces is to be expected.

We first discuss polar anion terminated surfaces. The (001) surface PDS is depicted in figure 1. Due to the fact that surface atoms lose two nearest-neighbour cations and four next-nearest-neighbour anions, a softening of the optical vibrational modes is to be expected and it should be more important for out of plane (z) vibrations than for in plane (x, y) vibrations. This is what is observed in figure 1. A shift of spectral weight from the optical region to the acoustical one is obtained for both compounds. The CdTe PDS is modified as a result of the introduction of the surface but the phonon gap remains unchanged for both vibration polarizations. By contrast, for out of plane vibrations the HgTe surface
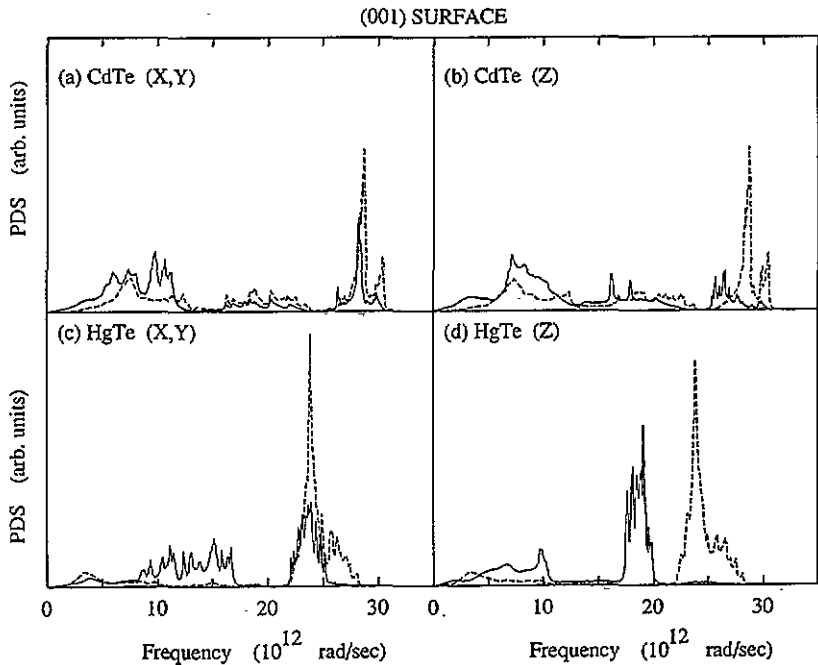
(001) SURFACE

Figure 1. The PDS of the anion terminated (001) surface: (a) CdTe, in plane vibrations; (b) CdTe, out of plane vibrations; (c) HgTe, in plane vibrations; (d) HgTe, out of plane vibrations. Solid line, surface plane; broken line, bulk anion plane.

PDS shows a strong shift of spectral weight from the optical branch to the bulk phonon gap (figure 1(d)), filling in this way the large phonon gap of the perfect crystal. This fact makes the HgTe (001) anion terminated surface a phonon gapless layer. Such behaviour is to be associated with the existence of surface localized optical phonon modes with a large dispersion in which anions are vibrating perpendicular to the surface. For the other polar anion terminated surface, (111), essentially the same behaviour is noted as for the (001) surface, as is shown in figure 2. Now each surface atom loses one nearest-neighbour cation and three next-nearest-neighbour anions, so that the perturbation associated with this surface should be weaker as compared to the previous case. This is observed in figure 2(a), (c), where it is clear that in plane (x', y') vibrations are very slightly affected by the surface for both compounds. However, the out of plane (z') PDS of the HgTe (111) surface layer presents large changes as compared with the bulk layer PDS. Figure 2(d) shows a large shifting of spectral weight of out of plane (z') vibrations from the optical region to lower frequencies, where resonance peaks appear in the form of spikes at the top of the bulk acoustical branch. A small phonon gap is now preserved between surface acoustical and optical branches.

A common feature of both polar anion surfaces, (001) and (111), we have analysed above is the unequal distribution of spectral weight among acoustical and optical branches in CdTe and HgTe. It is to be remembered that the mass of the anion (tellurium) $(211 \times 10^{-27}$ kg) takes an intermediate value between those of cadmium atoms and mercury atoms. As a consequence, the PDS of anion planes in bulk CdTe must have more spectral weight in the acoustical region than in the optical one. For HgTe, the opposite must be true.
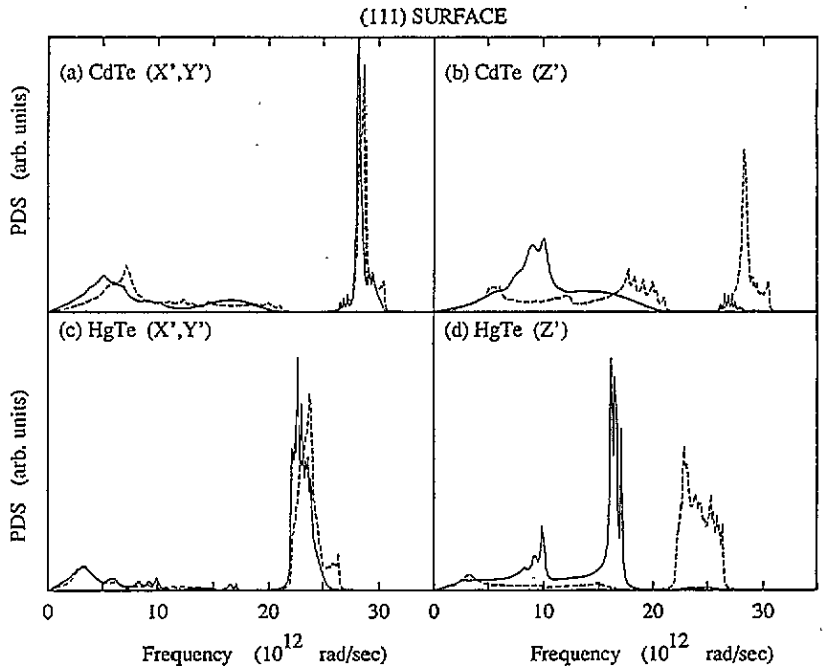
(111) SURFACE

Figure 2. As figure 1 but for the anion terminated (111) surface.
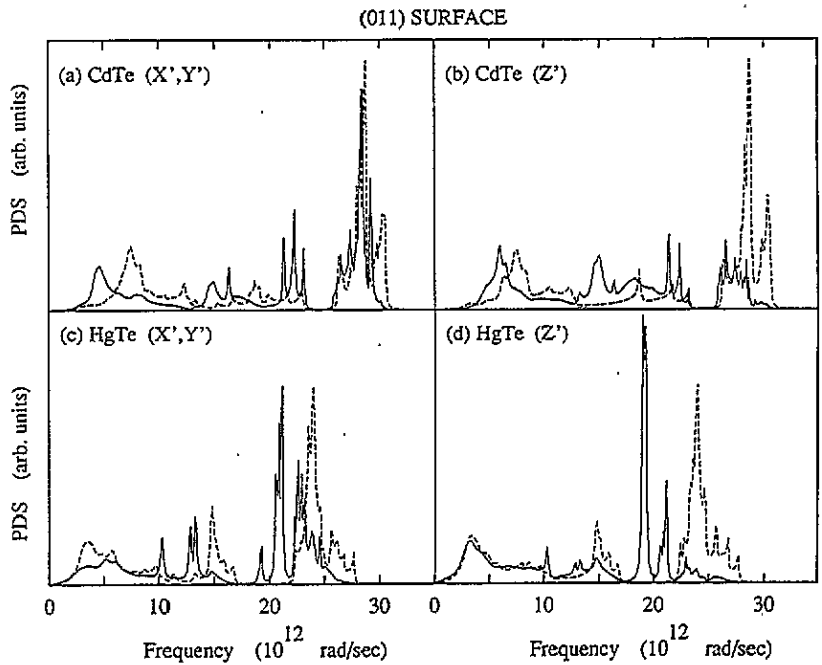
(011) SURFACE

Figure 3. As figure 1 but for the non-polar (011) surface.

In contrast to the previous two cases, the (011) surface is composed of an equal number of cations and anions, that is, it is a non-polar surface. Each atom in this surface loses one nearest-neighbour atom and five next-nearest-neighbour atoms. The PDSs for CdTe and HgTe are depicted in figure 3. A richer structure in the PDS is found, as compared with the polar surfaces. The non-polar CdTe surface (figure 3(a), (b)), shows both in plane (x', y') and out of plane (z') resonances at the top of the acoustical branch, a feature not occurring in the polar surfaces. However, the bulk phonon gap is still present. The HgTe surface (figure 3(c), (d)), presents highly localized vibrational modes with frequencies lying at the phonon gap of the bulk material. This HgTe surface is again a phonon gapless atomic plane.

It should be mentioned that there exists experimental evidence of reconstruction of clean CdTe surfaces, for the three surface orientations we consider here [17, 18]. Whether a surface reconstruction will result in substantial modification of the PDSs analysed above is yet to be determined. However, our work, which only describes ideal surfaces, can be considered to be the first step toward the understanding of the surface phonon structure of these important II–VI compound semiconductors.

3.2. Interfaces

Another kind of perturbation is present when an interface is built. The interface calculations have been performed assuming no lattice mismatch in the crystal structures of the CdTe and HgTe compounds. With this assumption, dramatic effects are seen at the common anion interface of the compounds we are interested in, as shown in figure 4 for the (001) interface case. It is worth pointing out that, while in bulk zincblende crystals the x, y and z vibrations are equivalent due to the cubic symmetry, at the interface layer in plane (x, y) and out of plane (z) vibrations present a very different spectrum. The first point to be noted is the dominance of HgTe acoustical modes at the interface layer. At higher frequencies the interface PDS exhibits features that are strikingly close to the persistent spectra, showing a marked two-mode behaviour. In addition, we find that, at the interface layer, new features in the frequency interval between the optical main peaks of both materials appear. In particular, peaks at frequencies in between those of the bulk main optical peaks are evident, for in plane as well as for out of plane vibrations. It is tempting to associate these new peaks, induced by the interface itself, to the not yet explained data reported in [7] occurring in the same spectral region. Finally, the interface atomic plane shows itself as a phonon gapless layer. This behaviour is similar, but less pronounced, to that found at the HgTe (001) surface. Thus we have a narrowing of the phonon gaps of CdTe and HgTe in a limited region near the interface, which allows us to conclude the existence of a phonon gapless zone around the (001) interface plane.

For the other polar interface, (111), it is necessary to distinguish two possibilities: (i) one Te atom bonded to three Cd atoms on one side and to one Hg atom on the other side; (ii) one Te atom bonded to one Cd atom on one side and to three Hg atoms on the other side. In any case it is no longer valid that x', y' and z' vibrations are equivalent in bulk materials, as is evident in figures 5 and 6, where in plane (broken line) and out of plane (solid line) bulk densities of vibrational modes are slightly different. For the first choice of tellurium bonding at the interface, the PDS calculated is plotted in figure 5. We notice, at the interface anion layer, features that are very different to the addition or persistent spectra, which are obtained by assuming a simple superposition of the PDS of each compound. Instead, the PDS we obtain appears to be rather peaked because of a new bonding of Te based tetrahedra at the interface. Similar features in the CdHgTe alloy PDS [16] have also been identified as associated with vibrations of an identical local atomic arrangement. Out of plane vibrations at the interface layer are located at frequencies corresponding to those
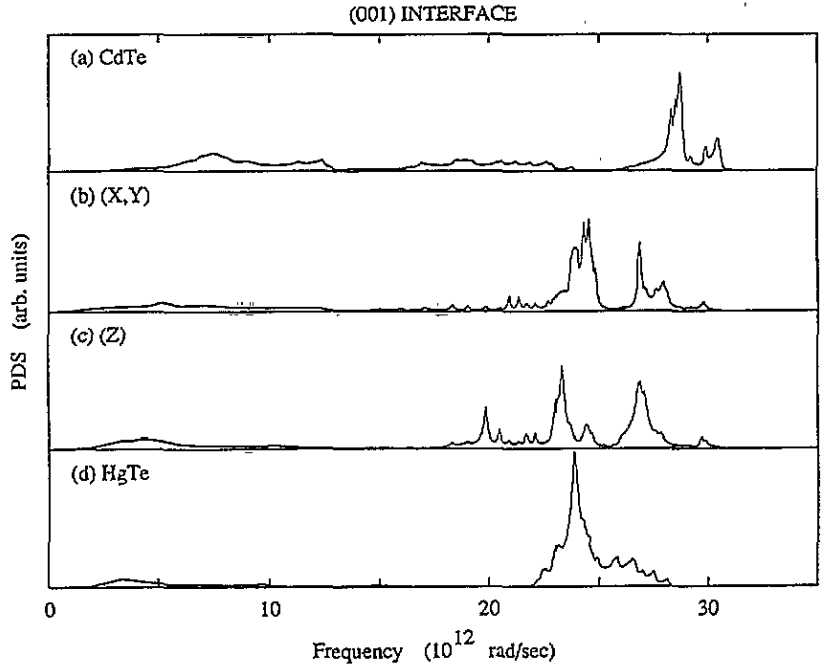
Figure 4. The PDS of anion planes for the (001) CdTe/HgTe interface. (a) CdTe bulk plane; (b) in plane vibrations at interface plane; (c) out of plane vibration at interface plane; (d) HgTe bulk plane.

of the HgTe compound, while in plane vibrations originate from CdTe optical features, although slightly down shifted. It is also interesting to note that at the second anion layer on either side of the interface the PDS is very near to the corresponding bulk result. This fact indicates that the interface induced effects vanish very quickly as one goes away from the interface. For the second interface Te bonding choice, the calculated PDS is depicted in figure 6. Now, the in plane vibrations of bulk HgTe are still present in the interface anion layer. The out of plane vibrations at the interface are mainly derived from CdTe vibrations. From figure 6 the existence of resonances at the top of the acoustical branch of bulk CdTe is also clear. These resonances are associated with vibrations perpendicular to the interface. As before, the new interface induced features are strongly localized, converging to the bulk values in about three anion layers at any side of the interface.

It is worth noting that the (111) interface phonon spectrum depends on the precise details of the chemical coordination at the interface: the interface PDS is very different for Te atoms surrounded by three Hg atoms and one Cd atom and conversely. In this regard, we note that the present method, despite its neglect of long-range forces, is clearly capable of accounting for local environment effects at the interfaces. A polarization dependent Raman measurement would be able to discern between these bonding situations at the (111) interface.

The PDS of the (011) non-polar interface is shown in figure 7. In this case there is no longer a common atomic plane between the two materials. The interface is then more abrupt than in the polar cases. This is evident in figure 7(b), (c), where it is shown that in plane and out of plane vibrations at the interface on the CdTe side are very different from
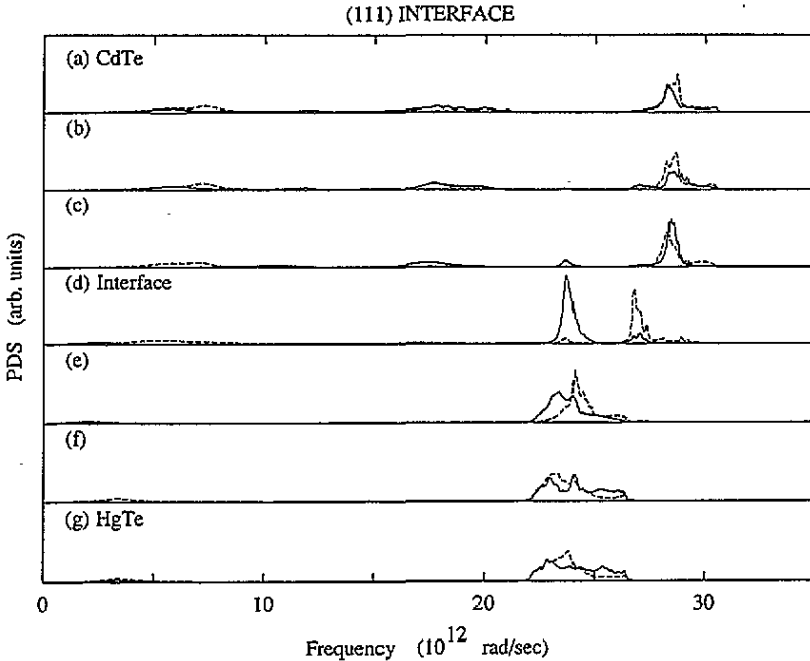
(111) INTERFACE

Figure 5. The PDS of anion planes for the (111) CdTe/HgTe interface in which three Cd atoms and one Hg atom are bonded to the same interface Te atom. (a) CdTe bulk plane; (b) second anion layer at the CdTe side from the interface; (c) first anion layer at the CdTe side from the interface; (d) interface anion plane; (e) first anion layer at the HgTe side from the interface; (f) second anion layer at the HgTe side from the interface; (g) HgTe bulk plane. Solid lines denote out of plane vibrations and broken lines in plane vibrations.

the corresponding vibrations on the HgTe side (figure 7(d), (e)). A two-mode behaviour is observed in the PDS of both interface layers, which also show no phonon gaps, in contrast with the bulk layers (figure 7(a), (f)). Thus we found a limited region near the interface that allows optical vibration modes of one material to penetrate into the other material over a short distance.

In view of recent developments in heterostructure growth techniques, whereby various growth parameters can be controlled (such as substrate orientation), we hope that the densities of phonon states obtained by the present method (and its modifications) would be helpful in the microscopic characterization of such interfaces using infrared or Raman measurements.

4. Conclusions

We have studied the vibrational properties of polar, (001) and (111), and non-polar, (011), ideal surfaces and lattice matched interfaces of the II–VI compounds CdTe and HgTe. We have shown how, using a simple dynamical matrix parametrization in the framework of the force constant model, a great deal of information can be obtained on the phonon spectra of these important materials. This is a relatively simple but powerful method by which both the bulk and surface phonon spectra of a semi-infinite crystal can be studied. The method can
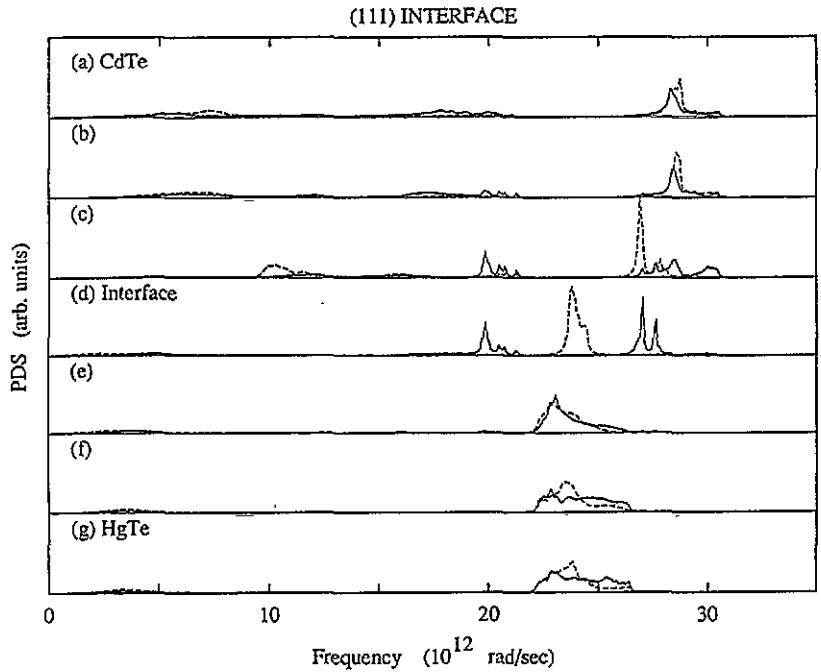
Figure 6. As figure 5 but for the (111) CdTe/HgTe interface in which one Cd atom and three Hg atoms are bonded to the same interface Te atom.

be generalized in a straightforward manner to study the vibrational structure of an interface formed by joining two semi-infinite crystals. We note that the layer phonon densities of states, evaluated by the GF method for different layer orientations, are useful in studying the effects of symmetry breaking, by a surface or interface, on vibrational properties, despite the neglect of long-range forces. Of the two compounds studied, HgTe is found to present phonon states near the surface drastically modified by the creation of the surface. (001) and (111) polar interfaces show very different vibrational properties: while the former exhibits a two-mode or persistent behaviour with a vanishing phonon gap for both in plane and out of plane polarizations, the latter exhibits a one-mode behaviour depending on the vibration polarization. For the (011) interface a two-mode behaviour is obtained, where bulk optical modes of one compound penetrate some distance into the other compound.

In addition, phonon local densities of states present interface induced effects in the frequency range where some previous resonant Raman scattering data in CdTe/HgTe superlattices have not been explained. For these latter systems, an apparently contradictory result concerning Raman data has been reported in the literature. In data reported in [6], for a superlattice grown on a (111) CdTe substrate, no HgTe modes are seen. By contrast, for a superlattice grown on a (001) substrate, data in [7] show no evidence of CdTe modes. Resonance effects have been invoked to partially solve this controversy. However, our results demonstrate that the phonon spectra of (001) and (111) single interfaces are already very different. According to the polarization dependent Raman measurement, CdTe/HgTe (111) single interfaces may manifest a CdTe- or HgTe-like feature. More careful resonance and polarization dependent Raman experiments on single- or multiple-interface CdTe/HgTe heterostructures have to be carried out in order to settle this point.
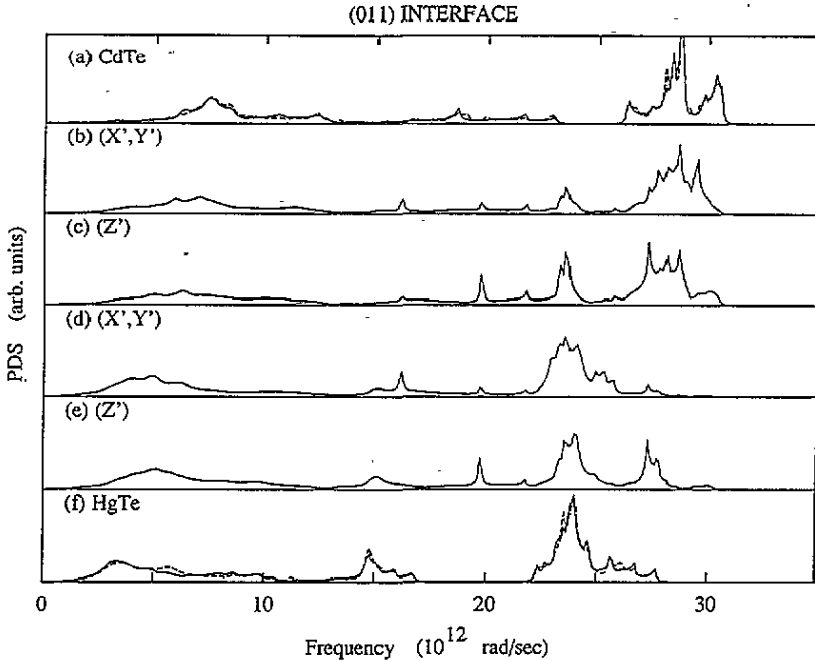
Figure 7. The PDS of polar planes for the (011) CdTe/HgTe interface. (a) CdTe bulk plane; (b) in plane vibration at the CdTe interface plane; (c) out of plane vibration at the CdTe interface plane; (d) in plane vibration at the HgTe interface plane; (e) out of plane vibration at the HgTe interface plane; (f) HgTe bulk plane. Solid lines denote out of plane vibrations and broken lines denote in plane vibrations for the bulk planes.

Finally, since the method we used in this work is flexible, it will be possible to incorporate realistic structural models dealing with surface reconstructions and interface alloying, when they become available, to calculate more accurate phonon structures of such surfaces and interfaces.

Acknowledgments

References

[1] Faurie J P 1986 *IEEE J. Quantum Electron.* **QE-22** 1656
[2] McGill T C, Wu G Y and Heltzer S R 1986 *J. Vac. Sci. Technol.* A **4** 20913
[3] Meyer J R, Hoffman C A and Bartoli F J 1990 *Semicond. Sci. Technol.* **5** S90
[4] Rey R, Quiroga L and Camacho A 1993 *J. Phys.: Condens. Matter* **5** (Supplement 33A) A203
[5] Rey-Gonzalez R, Quiroga L and Camacho A 1994 *Brazilian J. Phys.* **24** 106
[6] Olego D J, Faurie J P and Raccah P M 1985 *Phys. Rev. Lett.* **55** 328
[7] Feng Z C, Perkowitz S and Wu O K 1990 *Phys. Rev.* B **41** 6057

[8]   Dal Corso A, Baroni S, Resta R and de Gironcoli S 1993 *Phys. Rev.* B **47** 3588
[9]   Maradudin A A, Montroll E W, Weiss G H and Ipatova I P 1971 *Theory of Lattice Dynamics in the Harmonic Approximation, (Solid State Physics Supplement 3)* ed H Ehrenreich, F Seitz and D Turnball (New York: Academic)
[10] Lopez-Sancho M P, Lopez-Sancho J M and Rubio J 1984 *J. Phys. F: Met. Phys.* **14** 1205
[11] Rodriguez F J, Camacho A, Quiroga L and Baquero R 1990 *Phys. Status Solidi* b **160** 127
[12] Rodriguez F J, Camacho A and Quiroga L 1991 *Solid State Commun.* **77** 623
[13] Cunningham S L 1974 *Phys. Rev.* B **10** 4988
[14] Bilz H and Kress W 1979 *Theory of Phonon Dispersion Relations in Insulators (Springer Series in Solid State Sciences 10)* (Berlin: Springer)
[15] Kobayshi A 1985 *PhD Thesis* University of Illinois at Urbana-Champaign
[16] Zhou-Wu Fu and Dow J D 1987 *Phys. Rev.* B **36** 7625
[17] Lu P and Smith D J 1987 *Phys. Rev. Lett.* **59** 2177
[18] Lu P and Smith D J 1991 *Surf. Sci.* **254** 119