

## Transition from surface vibrations to liquidlike dynamics at an incompletely melted semiconductor surface

N. Takeuchi

*Istituto Nazionale di Fisica della Materia and Scuola Internazionale Superiore di Studi Avanzati, via Beirut 4, I-34014 Trieste, Italy;  
International Centre for Theoretical Physics, P.O. Box 586, I-34014 Trieste, Italy;  
and Instituto de Física UNAM-Laboratorio de Ensenada, Apto. Postal 2681, Ensenada, Baja California, Mexico*

A. Selloni

*Istituto Nazionale di Fisica della Materia and Scuola Internazionale Superiore di Studi Avanzati, via Beirut 4, I-34014 Trieste, Italy  
and Department of Physical Chemistry, University of Geneva, Geneva, Switzerland*

E. Tosatti

*Istituto Nazionale di Fisica della Materia and Scuola Internazionale Superiore di Studi Avanzati, via Beirut 4, I-34014 Trieste, Italy  
and International Centre for Theoretical Physics, P.O. Box 586, I-34014 Trieste, Italy*

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We present results of a first-principles molecular-dynamics simulation of the vibrational spectrum of a model semiconductor surface where, close to the bulk melting temperature  $T_M$ , the top bilayer becomes diffusive. The specific example chosen is Ge(111). In place of the ordinary surface vibrations, we obtain a spectrum more akin to that of a confined liquid. In particular, we predict a dramatic decrease in the intensity of high-frequency (bond-stretching) surface mode intensity, associated with a local melting-induced breaking of hard covalent bonds in the top bilayer. [S0163-1829(97)10516-1]

Phenomena such as surface melting, nonmelting, and blocked, or incomplete, melting, are now very well established both experimentally and theoretically.<sup>1</sup> The main evidence collected so far is, however, essentially confined to static properties. These include various structure factors and elastic-scattering intensities (x rays, low-energy electron diffraction, high-energy ion scattering), as well as electronic properties, all of which again mainly reflect averages over surface-atom configurations.

Nowadays, however, increasingly powerful techniques for inelastic surface spectroscopy are becoming available. The surface phonons at low and moderate temperature are being and have been extensively investigated, not only in metals, but also in semiconductors and insulators, by He scattering and by electron-energy loss spectroscopy (EELS).<sup>2</sup> The general question which we wish to address in this paper is what will happen to these surface phonon excitations if and when the surface, in particular a semiconductor surface, undergoes a thermally driven disordering phase transition, such as blocked, often called incomplete, melting<sup>1</sup> (blocking and incompleteness both referring to the lack of propagation of melting to the lower layers as  $T_M$  is approached).

The system of choice is a semiconductor surface, Ge(111), whose phase diagram is rather well documented, exhibiting in particular an interesting and controversial phase transition at 1040 K, i.e., only 170 K below the bulk melting temperature  $T_M=1210$  K.<sup>3</sup> Two conflicting pictures have been proposed for this phase transition. One, based on data such as x rays,<sup>4</sup> medium-energy ion scattering,<sup>5</sup> and EELS,<sup>6</sup> as well as on theoretical results provided by *ab initio* simulations,<sup>7</sup> is blocked, or incomplete, surface melting. In this picture, the topmost bilayer, crystalline with mobile adatoms up to 1040 K, turns laterally diffusive, quasi-liquid-

like, and metallic between 1040 K and  $T_M$ . The competing picture, which has been recently proposed to explain high-resolution He scattering results, is of an order-order transition of the top bilayer of Ge(111) roughly from a crystalline state with mobile adatoms, to another crystalline state without adatoms, but with an internal bilayer spacing reduced by about 10%.<sup>8</sup> In view of the possibility that accurate inelastic data on this surface might soon become available, it seems interesting to investigate what is the prediction for at least one of the scenarios proposed.

In this paper, we present *ab initio* simulation results for the atomic *dynamics* of Ge(111), demonstrating the evolution from well-defined surface phonons at room temperature to a diffusive liquidlike behavior of the first incompletely melted bilayer near  $T_M$ . Calculations were carried out within the framework of the Car-Parrinello *ab initio* molecular-dynamics (MD) scheme.<sup>9</sup> We have used a repeated slab geometry, each slab consisting of six layers of 16 Ge atoms, plus four additional Ge atoms, which at the beginning of the simulation, at low temperature, laid on top of the surface as adatoms. The bottom surface was saturated by 16 hydrogen atoms. Two consecutive slabs were separated by an empty space 7.6 Å wide. The five topmost layers of the slab and the adatoms were given full freedom to move, while the sixth layer of Ge and H atoms were held fixed at the ideal positions, to simulate a bulklike termination. Other computational details are as in Ref. 7. The starting configuration for the simulation was the  $c(2\times 8)$  adatom structure of Ref. 10. This was first heated to  $\sim 600$  K, and after a brief ( $\sim 1.5$  ps) run at this temperature, during which the adatom structure became partly disordered,<sup>11</sup> we increased the temperature up to  $T=1200\pm 150$  K. The simulation was performed within the canonical ensemble, by using two independent Nosé ther-

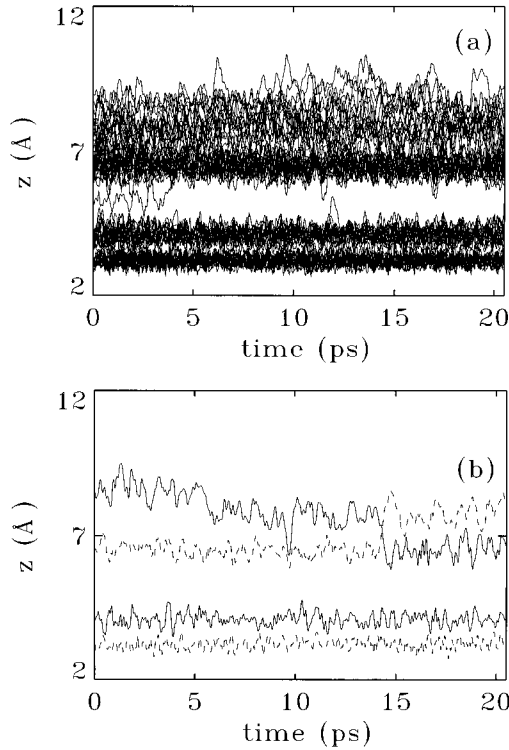


FIG. 1. (a) Time evolution of the  $z$  coordinates (perpendicular to the surface plane) for the atoms in the first and second bilayers of the Ge(111) slab at  $T \sim T_M$ . The second bilayer remains crystalline, but the first bilayer becomes diffusive. (b)  $z(t)$  of selected atoms (Ref. 7) of the first and second bilayers, illustrating interchange processes of two atoms between the top and the bottom regions in the first bilayer but not in the second.

mostats, one coupled to the ions and the other to the electrons according to the prescription in Ref. 12. We carried out the simulation for a total of 21 ps. Data were finally taken from trajectories within the last 13 ps, when the system was in reasonable equilibrium.

Figure 1 shows the time evolution of  $z$  coordinates for the two outermost surface bilayers of Ge(111) at  $T \sim T_M$ . We note that while the second bilayer is still crystalline, all atoms vibrating around their equilibrium positions, what used to be the first crystalline bilayer, is now positionally disordered. In this region atoms diffuse laterally as a function of time, and also exchange vertically, although with a slower rate, between the top and bottom of the bilayer [Fig. 1(b)]. This behavior is compatible with expectations for an incompletely melted surface.

In order to study quantitatively the dynamical properties of this surface, we calculated the *layer-resolved* vibrational spectral density, or projected density of vibrational states, by taking the Fourier transform of the velocity-velocity autocorrelation functions

$$D_{\alpha,\alpha}^{(l)}(\nu) \propto \int_0^\infty Z_{\alpha,\alpha}^{(l)}(t) \cos(2\pi\nu t) dt, \quad (1)$$

where

$$Z_{\alpha,\alpha}^{(l)}(s) = \sum_i \langle v_{i,\alpha}^{(l)}(t) v_{i,\alpha}^{(l)}(t+s) \rangle. \quad (2)$$

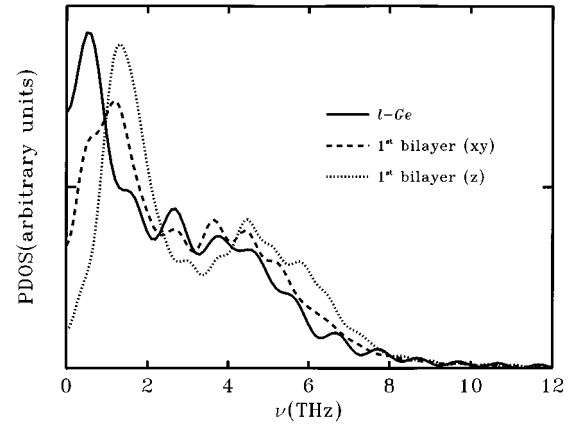


FIG. 2. Calculated vibrational density of states for the first bilayer of Ge(111) at  $T \sim T_M$ , compared to that of bulk liquid (full line) Ge at  $T \sim 1500$  K (from Ref. 13). The dashed (dotted) curve refers to motion in (perpendicular to) the surface plane.

Here  $v_{i,\alpha}^{(l)}$  are the instantaneous position, and the  $\alpha = x, y, z$  component of the velocity of the  $i$ th atom belonging to layer  $l$ .

Figure 2 shows  $D_{z,z}(\nu)$  and  $D_{\parallel}(\nu) = \frac{1}{2}(D_{x,x} + D_{y,y})$  for the *first* bilayer ( $z$  is the direction perpendicular to the surface) obtained at  $T \sim T_M$ . For comparison we also plot the same spectral density for a slice of bulk liquid Ge at  $T \sim 1500$  K, taken from a recent independent first-principles MD simulation.<sup>13</sup> By contrast, Fig. 3 shows  $D_{z,z}(\nu)$  and  $D_{\parallel}(\nu)$  for the *second* bilayer, now compared with the phonon density of states for bulk crystalline Ge at  $T \sim T_M$ . The latter was independently obtained from a separate MD simulation with a bulk supercell of 96 Ge atoms, and with the same symmetry of the surface calculations.

In crystalline bulk at room temperature, the major density of states peaks are known to fall at roughly 9 and 2.5 THz,<sup>14</sup> corresponding to bond-stretching optical modes, and to bond-bending zone-boundary acoustical modes, respectively. Our previous bulk simulation at  $T \sim 300$  K (Ref. 15) yielded peaks in excellent agreement with these experimental ener-

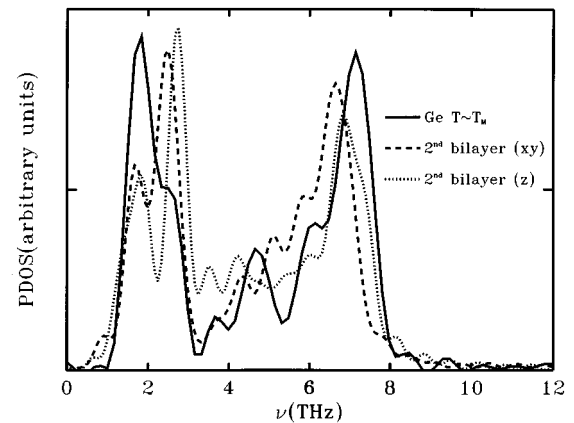


FIG. 3. Calculated vibrational density of states for the second bilayer of Ge(111) at  $T \sim T_M$ , compared to that of bulk solid Ge (full line) at the same temperature. The dashed (dotted) curve refers to motion in (perpendicular to) the surface plane.

gies. In our newer bulk crystal simulation at  $T \sim T_M$ , these spectral peaks are anharmonically redshifted to  $\sim 7.5$  and  $\sim 1.8$  THz.

Coming to the warm (111) surface at  $T \sim T_M$ , we find, not surprisingly, that in the *second bilayer* (Fig. 3) the density of vibrational states is close to that of the bulk solid at the same temperature. In detail, however, there is a small additional redshift by about 0.5 THz of the high-frequency bond-stretching modes (mostly of the  $x,y$  polarization), and a strong increase of intensity near 2.6 THz, which is the high-energy side of the bond-bending peak.

By contrast,  $D_{z,z}$  and  $D_{\parallel}$  for the first and outermost surface bilayers (Fig. 2), now exhibit features different from the crystal, and instead quite close to those of the bulk liquid. In particular, the high-frequency bond-stretching peak has essentially collapsed, leaving in its place only a weaker broad remnant, again mostly polarized along  $z$ , centered around  $\sim 5$  THz, with a large width of perhaps  $\sim 2-3$  THz. This remnant can be related to the existence of well-defined vertical covalent bonds which still connect second and third layers. The mean characteristic stretch frequency reduction from 7.5 to  $\sim 5$  THz, is plausibly explained in terms of severe *doping* of the covalent bonds due to proximity of the metallic diffusive first bilayer. The large broadening found is also in agreement with this explanation, since mobile electrons in these doped bonds should, roughly speaking, pump in and out when the bond vibrates, and thus give rise to a damping of similar magnitude to the shift.

At the opposite, low-frequency side, the  $(x,y)$  surface spectral intensity at  $\nu=0$  is smaller than that of  $l$ -Ge, clearly reflecting a factor of about 2 between the bulk-liquid diffusion coefficient at the melting point, estimated to be  $\sim 8$  in units of  $10^{-5}$  cm<sup>2</sup>/s and the melted bilayer mean value, of  $\sim 3.5$ .<sup>7</sup> The  $z$ -polarized spectral intensity, on the other hand, is very small at  $\nu=0$ , reflecting the essential *confinement*, quite evident from Fig. 1, of the diffusive bilayer along the surface normal.

Finally, we find sizable low-frequency spectral peaks near 1.3 THz, more pronounced in  $z$  motion, but also present for  $x,y$  motion. This feature, which is absent in bulk-liquid Ge, reflects slow oscillations of atoms in the strongly layered quasiliquid region.

We should stress here that severe geometrical limitations in our calculation do not permit a study of the fate of proper surface acoustical vibrations, at an incompletely melted semiconductor surface. The microscopic thickness of the quasiliquid bilayer, however, suggests that premelting effects on these modes, at least at relatively large wavelengths, could be minor.

In conclusion, we have identified well-defined dynamical signatures, mainly a liquidlike collapse of the high-frequency stretching modes, which a high-temperature semiconductor (111) surface, typified by Ge(111), should show if it is incompletely melted just below  $T_M$ . As for the alternative possibility of an ordered structure, we have not been able to identify a reasonable starting point for its simulation. However, if indeed the surface did manage in some way to retain crystalline order and rigid covalent bonds in that regime, their characteristic stretching frequencies around  $\sim 7.5$  THz should presumably still show up very strongly at the surface, right up to  $T_M$ . We hope that future surface inelastic scattering measurements will become available in order to check either of these predictions.

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