

Temperature dependence and stability of surface structures

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Burton and Jura have reported a calculation that predicts a structural phase transition for the (100) surface of an fcc crystal. Although the calculation was for Ar, one might expect such a transition to be possible for other fcc materials. However, we find that a structural transition of the kind predicted is impossible, because the rearranged structure is unstable.

Several years ago, Burton and Jura¹ reported a calculation that was based on an Einstein model and that predicted a structural phase transition for the (100) surface of Ar. On the basis of this calculation, one might expect to be able to observe such a surface phase transition in noble-gas solids² and other fcc materials, such as Al and Ni. We show in Fig. 1(a) the unrearranged fcc (100) surface, and in Fig. 1(b) the rearranged surface that is predicted at high temperatures in the calculation of Ref. 1. In the rearranged structure, every other row of atoms has been displaced by half the edge of a square in the x direction.

In order to study the possibility of this structural transition, we performed a lattice-dynamics calculation of the vibrational frequencies for the rearranged structure. The calculation involved the usual procedure,³ with the only complication being that there are two particles per unit cell. We used a Lennard-Jones potential of interaction between the atoms, as in Ref. 1, and we did the calculation for an 11-layer slab. (As a check, we also used smaller thicknesses and found that the results reported here are not much affected by the finite thickness of the slab.) Preliminary to calculating the vibrational frequencies, we allowed the rearranged and unrearranged atoms in the surface [represented, respectively, by the solid and open circles of Fig. 1(b)] to relax outward, taking the atoms in the second, third, etc., layers to remain in their bulk positions. The outward relaxation was found to be $0.213a$ and $0.036a$ for rearranged and unrearranged atoms, respectively, where $\sqrt{2}a$ is the nearest-neighbor spacing in the bulk.

In Fig. 2, we show the dispersion curves from the origin to the edge of the surface Brillouin zone in the q_x direction. Near the origin, for a pair of modes localized near the surface, the vibrational frequency ω becomes imaginary; i. e., $\omega^2 < 0$ for sufficiently small values of q_x . Imaginary frequencies correspond to an instability, so this result implies that the rearranged structure is mechanically unstable.

In Fig. 3, we show the eigenvector component ξ_x for the modes with $\omega^2 < 0$ at $q_x = 0$. We have

plotted the average value of $\text{Re}\xi_x$ as a function of layer number for the pair of modes associated with the instability. (These modes are almost identical; as usual, there are two surface modes of each type because the slab has two identical surfaces.) For these modes, $\xi_y = \xi_z = \text{Im}\xi_x = 0$. It can be seen that the instability is associated primarily with motion of the rearranged particles at the surface in the x direction. We thus have the result that at long wavelengths (small q_x) the rearranged atoms move back to their unrearranged positions, i. e., they "slide off" the atoms in the second layer back into the "holes" corresponding to the unrearranged positions. As short wavelengths (larger values of q_x), the instability is removed and $\omega^2 > 0$, presumably because the atoms are not vibrating in phase and an atom which tries to "slide off" into the "hole" that it came from will encounter another atom. Only for wavelengths bigger than about ten

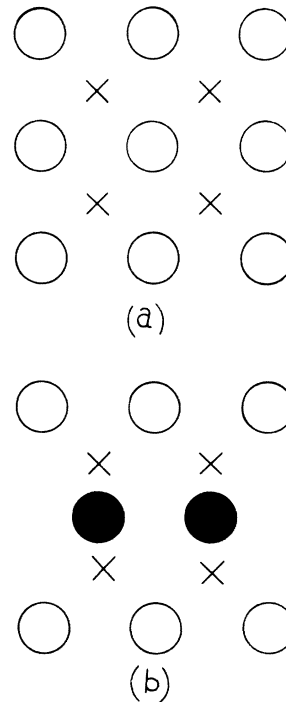


FIG. 1. (a) Unrearranged (100) surface of fcc crystal. (b) Rearranged surface. Open circles represent unrearranged surface atoms, solid circles represent rearranged surface atoms, and x 's represent atoms in the next plane beneath the surface. The arranged atoms in (b) are above the unrearranged atoms (see text).

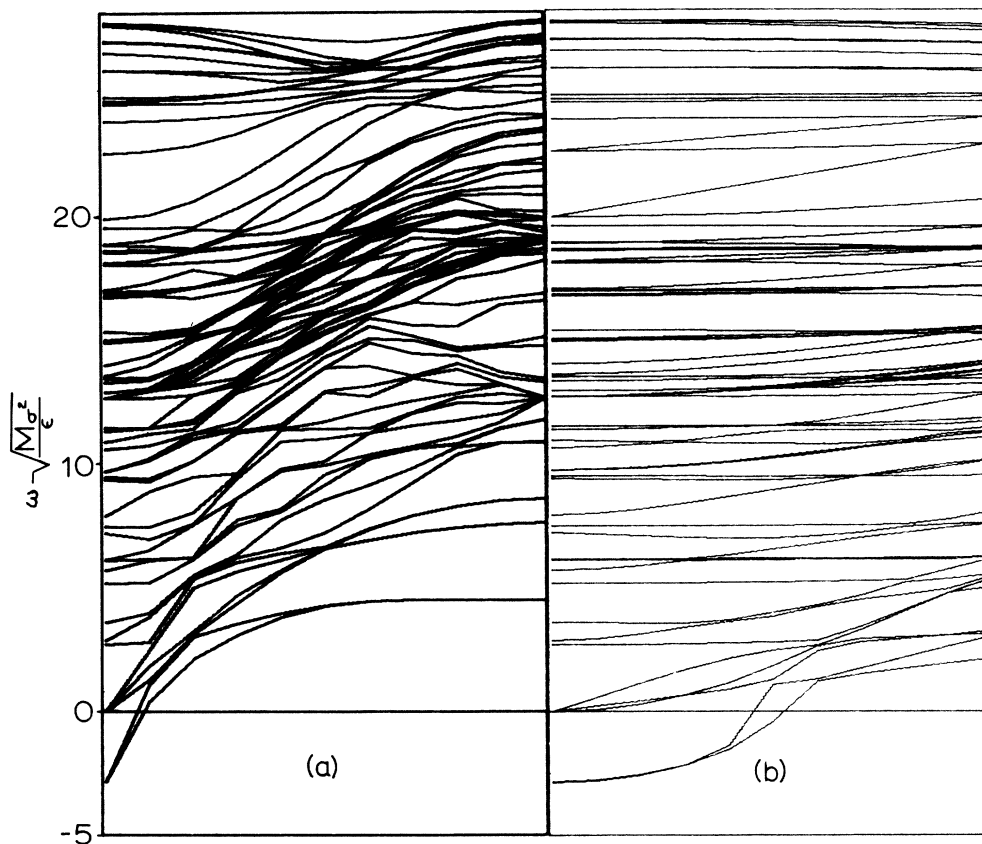


FIG. 2. (a) Dimensionless vibrational frequencies from the origin to the edge of the surface Brillouin zone in the q_x direction. Here ω is the frequency, M is the atomic mass, and σ and ϵ are the Lennard-Jones potential parameters. If $\omega^2 > 0$, we plot the real part of ω above the horizontal axis; if $\omega^2 < 0$, we plot the imaginary part of ω below this axis as a negative number. The calculation was done for 11 values of q_x , and no attempt was made to connect the lines properly in the event of crossovers. (b) Dimensionless frequencies from the origin to a point one-fifth of the way to the edge of the surface Brillouin zone, showing in more detail how ω becomes imaginary as $q_x \rightarrow 0$ for the pair of surface modes associated with the structural instability.

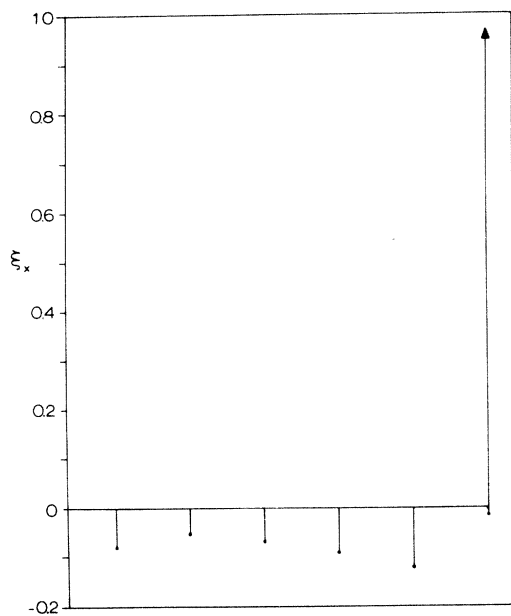


FIG. 3. ξ_x vs layer number for the modes with $\omega^2 < 0$ at $q_x = 0$ in Fig. 2. The surface layer is at the extreme right, and the sixth layer (i.e., middle layer of the 11-layer slab) at the extreme left. In all but the surface layer, ξ_x is almost exactly the same for both particles in the unit cell (i.e., for $\kappa = 1$ or 2 in the notation of Ref. 3). In the surface layer, the large value of ξ_x marked with an arrow corresponds to the rearranged particles, and the small value marked with a dot to the unrearranged particles.

atomic spacings (i. e., q_x smaller than one-tenth the distance to the Brillouin zone edge in Fig. 2) is $\omega^2 < 0$. [We mention that we have also performed calculations for the two rearranged (110) surfaces suggested in Ref. 1 (see Fig. 4 of this reference), and they are even more unstable than the rearranged (100) surface.]

The conclusion to draw from the above results is that one cannot do just a thermodynamic treatment using, for example, an Einstein model in treating the possibility of structural phase transitions. One must also consider the stability of the proposed structures.

¹J. J. Burton and G. Jura, in *The Structure and Chemistry of Solid Surfaces*, edited by G. A. Somorjai (Wiley, New York, 1969).

²A. Ignatiev and T. N. Rhodin, *Phys. Rev. B* 8, 893

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³R. E. Allen, G. P. Alldredge, and F. W. de Wette, *Phys. Rev. B* 4, 1648; 4, 1661 (1971).