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Thermal expansion of Ag(111)

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The contribution of surface vibrations to the thermal expansion of Ag(111) is analyzed at several levels of approximations. In the quasiharmonic scheme, the surface vibrational density of states, which may be represented fairly by modes at the high symmetry points in the surface Brillouin zone, do not lead to anomalously large thermal expansion, in accordance with results from molecular-dynamics simulations that give a good description of other anharmonic properties of Ag(111). We illustrate how an inadequate representation of the density of states can lead to erroneously large surface thermal expansion. [S0163-1829(97)51716-4]

One of the simple manifestations of the presence of a surface is a relaxation of the outer layers of atoms either inwards or outwards with respect to the bulk terminated positions. For the (111) surface of fcc metals, however, these relaxations are expected to be minimal, since the loss of neighbors is lower than that on the other two low Miller index surfaces. Also, because of its compactness the fcc(111) surface is expected to show little charge smoothing of the type predicted by Smoluchowski[1] and hence a small surface relaxation according to conventional thinking.[2] In fact experimental observations and theoretical calculations of relaxations on the (111) surface of a number of metals show that the effect is indeed very small,[3] particularly when compared to the more open (110) surface. As the temperature increases, anharmonic effects that are known to be larger at the surface than in the bulk[4] become increasingly important. Beyond a characteristic temperature, surface vibrations also display the onset of enhanced anharmonicity[5] that may further manifest itself as unexpectedly large surface thermal expansion,[6,7] surface disordering, roughening, and/or premelting.[8,9] However, these dramatic effects have been found mainly on the (110) and, to a lesser extent, on the (100) surfaces of several fcc metals. By contrast, the (111) surface of these metals has been predicted in atomistic theoretical calculations[10] to remain stable almost up to the bulk melting temperatures. The recent results for the thermal expansion of Ag(111) (Ref. 11) and Cu(111) (Ref. 12) are, therefore, surprising. Using medium energy ion scattering (MEIS), Statiris *et al.*[11] observed a small contraction of the outer layers of Ag(111) (the surface interlayer separation d_{12} was found to be reduced by 2.5%) at low temperatures and continuing to 670 K (about half the bulk melting temperature of silver). After this temperature, d_{12} increased dramatically from 0% relaxation at 750 K to 10% *expansion* at 1150 K (about 80 K below the bulk melting temperature). For Cu(111) the effect is not so pronounced, yet there is an overall outward thermal expansion of 5.3% between 300 K and 1180 K.[12]

Using a many-body interaction potential based on the embedded atom method (EAM) (Ref. 13) to describe the interaction between the Ag atoms, Lewis[14] has simulated the thermal behavior of Ag(111) for a large range of temperatures to find that the outer layer remains contracted (i.e., d_{12} is less than the bulk value) up to 1100 K. We have also performed similar molecular-dynamics (MD) simulations of Ag(111) and do not observe a reversal of the sign in the relaxation up to 1100 K. By calculating the structure factor and the orientational order parameter, we find that the Ag(111) surface stays well ordered and crystalline at all temperatures up to 1100 K.[15] Since conclusions about the temperature dependence of d_{12} from these two calculations based on EAM potentials are not in qualitative agreement with those extracted from the analysis of experimental data, it is plausible to suggest that the EAM lacks the necessary ingredients for describing the complex nature of the anharmonic parts of the interaction potential. After all EAM is an empirical, and not an *ab initio*, method and simplifying assumptions have been made about the nature of the charge densities in solids. Nonetheless it is still puzzling that MD simulations based on EAM potentials would do such a bad job of mimicking the surface thermal expansion of Ag(111) when they yield not just qualitative *but also quantitative* agreement for the temperature dependence of the mean-square displacement of the surface atoms of Ag(111)[15] to that extracted from the very same MEIS data.[11] The anharmonicity in the interaction potential that controls the variation with temperature of the mean-square displacements should also control the temperature dependence of the thermal expansion coefficient. Furthermore, similar MD simulations for Ag(110) (Ref. 16) and Ni(100) and Ni(110) (Ref. 7) have led to good agreement with the data on the temperature dependence of the structure and the dynamics.

To address the issue of the anomalously large expansion of Ag(111), very recently, a tentative explanation was given by Narasimhan and Scheffler.[17] These authors evaluate $d_{12}(T)$ by minimizing the free energy of the system, with respect to d_{12}, in the quasiharmonic approximation. The static internal energy of the system and vibrational frequencies, corresponding to the three degrees of freedom of the plane containing the first layer atoms on a rigid substrate, were calculated using a first-principles electronic structure calculation based on nonlocal pseudopotentials and density functional theory in the local-density approximation. With this approach, they found d_{12} to increase significantly at high temperatures to about 15% at $0.9T_m$, in excellent agreement with the experimental observations.[11] It was argued that the rapid softening of the two inplane modes with temperature led to the large increase in d_{12}. The large softening of the modes was itself related to the rapid decrease of the corrugation in the potential with increasing d_{12}. It was also suggested that it is the lack of this feature in the interaction potential that prevents the EAM from yielding a large thermal expansion. Furthermore, by extending these model calculations to Al(111) it was predicted that the extent of the in-plane surface anharmonicity was material specific. More recent MEIS data on Cu(111) (Ref. 12) rely heavily on the interpretation presented by these model calculations and offer the relatively smaller thermal expansion of Cu(111), as compared to Ag(111), as further evidence of the validity of these theoretical results.

We have a fundamental difficulty with the picture that has emerged from these papers about the reason for the anomalously large thermal expansion on Ag(111) [and a somewhat smaller amount on Cu(111)]. Our main concern is with the assumptions in the theoretical model about the vibrations of the system. As is well known, the vibrational free energy depends on the phonon density of states that includes all types of modes. These modes are collective excitations of the system and exhibit various types of coupling between displacements of atoms in different layers and also within a layer. Since the calculation of the full vibrational density of states using first-principles methods is not yet feasible for transition metal surfaces, simplifications such as the frozen phonon method or the planar force-constant method[18] have been introduced to extract frequencies of modes at certain high symmetry points in the Brillouin zone. For Ag(111) the three vibrational modes that Narasimhan and Scheffler calculated correspond to the modes at the Brillouin zone center for the first layer on a *rigid* substrate. Thus even for this simple picture of the metal surface, modes corresponding to relative displacements of first layer atoms (corresponding to high symmetry points in the Brillouin zone boundary) are ignored. For Ag(111), as for other surfaces, these modes at the zone boundaries have well-defined characteristics[19] that in turn are representative of the changes in force fields that the atoms at the surface are subjected to, as compared to their bulk counterparts. It would seem reasonable that these zone boundary modes would play a role in determining the vibrational free energy of the surface.

So here is the puzzle. Narasimhan and Scheffler get good agreement with the data on thermal expansion by using the quasiharmonic approximation in a simple model for surface vibrations, and by ignoring zone boundary modes. MD simulations, which in principle include *full dynamics* and *full anharmonicity,* do not yield this large thermal expansion, even though it predicts the same temperature dependencies of the mean-square displacements as found in the experimental data. Is this a failure of the EAM? Or is the large thermal expansion an artifact of the model calculation? The aim of this paper is to address these and related questions by examining the contributions of the different parts of the phonon spectrum to the vibrational free energy of Ag(111). We begin with an evaluation of the phonon density of states and other thermodynamic properties of Ag(111) at 0 K using EAM potentials. We then proceed with a quasiharmonic calculation, with EAM potentials, following closely the recipe provided by Narasimhan and Scheffler. We discuss first the case in which we include vibrational contributions from first layer modes at the zone boundary in addition to those at the zone center. Next we present the case with only the zone center modes.

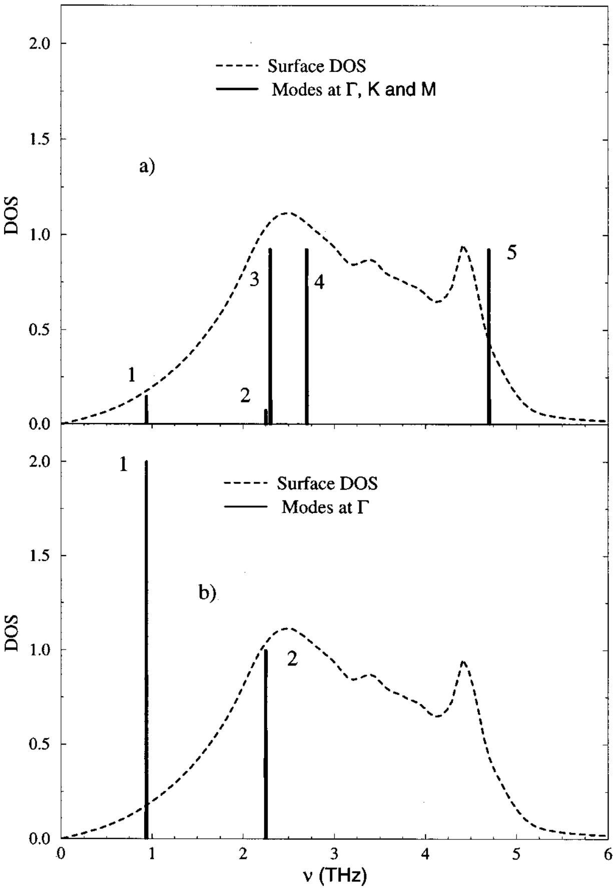

FIG. 1. Surface vibrational density of states for Ag(111) at 0 K (dashed lines). Also shown are approximate DOS with (a) five surface modes and (b) modes 1 and 2 only.

We determine the equilibrium configuration of Ag(111) at 0 K by minimizing the potential energy to find that d_{12} is contracted by 1.35% and d_{23} is not changed from the bulk value, in reasonable agreement with the 2% contraction reported by the MEIS (Ref. 11) data and first-principles calculations.[17] For this equilibrium configuration at 0 K, we calculate the surface vibrational density of states (DOS) using a real-space Green's-function approach[20,21] with force constants calculated using EAM. The resulting DOS, as presented in Fig. 1(a), leads to a zero point energy of 18.9 meV per surface atom in the harmonic approximation. For increasing temperatures a quasiharmonic approximation would involve calculation of the DOS for the expanded lattice at each temperature. Not only is this approach tedious and unnecessary for our purpose, since we already have information from the fully anharmonic calculation using the MD simulations, it does not allow us to compare our EAM results with those based on parameters from a first-principles calculations.[17] In the spirit of the latter we now look for a finite number of modes of the system and examine how well they depict the calculated DOS in Fig. 1(a). Using a ''frozen phonon'' method in which the top layer atoms are displaced from their equilibrium configuration according to predetermined patterns characteristic of surface layer modes at specific points in the Brillouin zone, while atoms in all other layers are held fixed, we calculate the frequencies of five modes labeled 1–5 in Fig. 1(a). Here mode 1 and 2 are zone-center modes (Γ

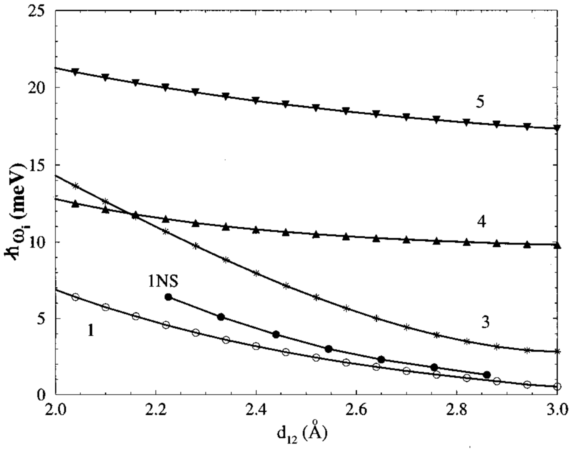

FIG. 2. Variation of the energy of modes 1, 3, 4, and 5 with d_{12}. The curve labeled 1NS is taken from Ref. 17 for comparison.

point) and correspond to the displacement of the top layer in the in-plane and vertical directions, respectively. Due to the equivalency of the two in-plane directions, mode 1 is doubly degenerate. The modes labeled 3, 4 and 5 represent, respectively, the frequencies of the shear vertical (SV), shear horizontal (SH), and the longitudinal (L) modes at the surface Brillouin zone boundary $\bar{M}$.[22] At this zone boundary, the frequencies 2.3 THz, 2.7 THz, and 4.7 THz of the SV, SH, and L modes, respectively, are in excellent agreement with values obtained from first principle calculations.[19] From symmetry considerations, each of these modes is 12 times degenerate. The weights of these five modes are then: 2/13 for mode 1, 1/13 for mode 2, and 12/13 for modes 3, 4, and 5. From Fig. 1(a) it appears that these five modes with the above weights give a fairly good description of the true DOS, even under the drastic assumption of a rigid substrate. The corresponding zero point energy turns out to be 19.1 meV, very close to the one determined by the full DOS. If, however, instead of the five modes we consider only the zone-center modes (modes 1 and 2 with weights 2 and 1, respectively), we can see in Fig. 1(b) that the DOS is represented very poorly. As a matter of fact, mode 1 (motion of the top layer parallel to the surface) is terribly overweighted in this scenario. With modes 1 and 2, we find a zero-point energy of 8.55 meV, which is less than one-half of the value obtained with the full DOS.

Next, we calculate the dependence of the frequencies of modes 1, 3, 4, and 5, discussed above, on the interlayer separation d_{12}. Using the general recipe outlined by Narasimhan and Scheffler[17] and giving the top layer atoms small displacements of up to 0.15 Å along directions dictated by the polarization of the mode, these frequencies are calculated for a range of values of d_{12}. The results are presented in Fig. 2, which also includes the result from Ref. 17 for mode 1 (here labeled 1NS), for comparison. Mode 2 is not shown here, since in this simple picture, the dependence of its energy on d_{12} can be calculated quite easily by solving quantum mechanically the 1D anharmonic system, as shown earlier.[17] It is clear from Fig. 2 that mode 1 (based on EAM) softens in a manner similar to mode 1NS (based on first-principles calculations). Mode 3 also displays a dramatic softening, while the frequencies of modes 4 and 5 exhibit a much smaller dependence on d_{12}.

Now we turn to the calculation of $d_{12}(T)$ with the inclusion of the vibrational dynamics in the free energy. The free energy of the system as a function of d_{12} is given by

$$F(d_{12},T)=E_{stat}(d_{12})+\sum_{i=1}^{N} F_{vib}^{i}(d_{12},T) \qquad (1)$$

$$F_{vib}^{i}(d_{12},T)=c_i k_B T \ln\left\{2\sinh\left(\frac{\hbar\omega_i(d_{12})}{2k_BT}\right)\right\}, \qquad (2)$$

where k_B is the Boltzmann constant, $\hbar$ is Planck's constant c_i is the weight of mode i, and N is the number of modes included in the calculation.

The phonon contributions are included in three stages: (i) only z motion of the top layer (mode 2) in the fully anharmonic 1D system; (ii) modes 1 and 2 in the quasiharmonic approximation; and (iii) all five modes in the quasiharmonic approximation. The results are presented in Fig. 3, which also includes the data from previous MD simulation.[15] Note that d_{12} in this case starts with a contraction of 1.35% and increases with temperature to a zero relaxation at $0.9T_m$. For the first stage described above, d_{12} starts at low temperatures with a contraction of about 1.8% and increases steadily and reaches an expansion of about 1.2% at $0.9T_m$. In the case of stage 2 for which the weights c_i are 2 for mode 1 and 1 for mode 2, d_{12} starts with a contraction of about 1.4% at low temperature, increases steadily up to $0.7T_m$, where d_{12} is 10%, and then start diverging after $0.75T_m$. Finally, for stage 3, using the weights, 2/13 for mode 1, 1/13 for mode 2, and 12/13 for modes 3, 4, and 5, at low temperatures there is a contraction of 1.65% and the interlayer separation increases and crosses zero relaxation at about $0.36T_m$ and at $0.9T_m$, d_{12} has an outward relaxation of about 3.6%.

We note from Fig. 3 that when more vibrational modes are included in the evaluation of the free energy, d_{12} does not diverge anymore. The large increase in d_{12} in stage 2 above is also understandable. As the frequency of the in-plane modes becomes vanishingly small with increasing temperature while their weight stays finite (2 in this case), the Helmholtz free energy diverges. When more modes of higher weight (because of symmetry) are included in the DOS, the weight of the in-plane modes at $\bar{\Gamma}$ drops to 2/13 and the free energy no longer diverges to the melting temperature.

In summary, we have calculated the relaxation of the Ag(111) top layers using several approaches with EAM potential for the interaction between the Ag atoms. The calculations ranging from a fully anharmonic method using molecular dynamics to a more approximate one based on calculated free energies in a quasiharmonic treatment, do not yield an anomalously large outward thermal expansion for Ag(111). The MD simulations, on the other hand, provide excellent agreement with the experimental data for the temperature dependence of the mean-square displacement of the Ag(111) surface atoms. If, however, only the zone-center modes are included in the quasiharmonic calculations, our calculations just like that of Narasimhan and Scheffler[17] based on parameters extracted from first-principles calcula-

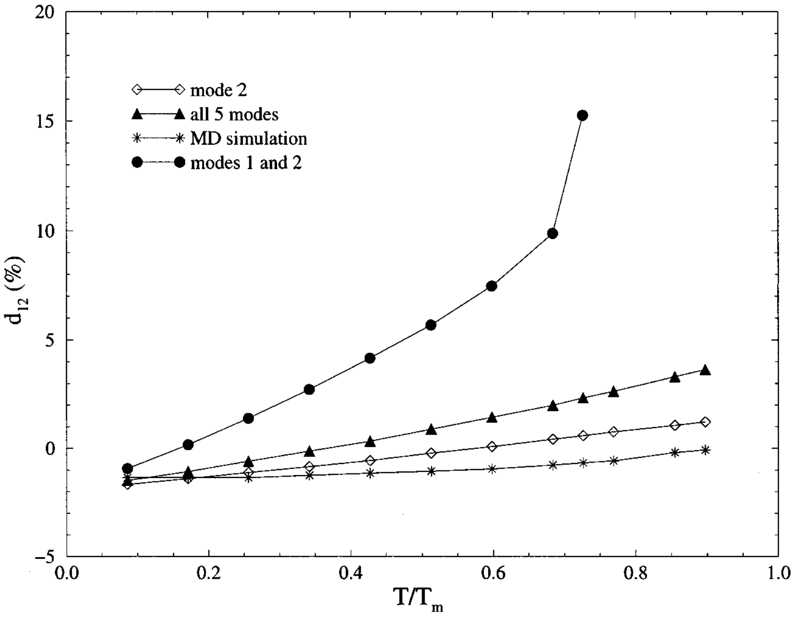

FIG. 3. The interlayer separation d_{12} versus temperature calculated by several different models.

tions, produce as large a thermal expansion as proposed in the MEIS data.[11] We have shown here that this is an artifact in the calculation arising from an improper representation of the vibrational density of states. What then causes the observed large thermal expansion of Ag(111)? So far, theoretically there is no answer. All calculations to date point to a small thermal expansion. Perhaps the better question to ask is does Ag(111) really have a large thermal expansion? Experimental data from other techniques are needed to have confidence in the answer.

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[22] From symmetry arguments, for the simple picture in which only the top layer Ag(111) atoms are dynamic, modes 3, 4, and 5 are also the frequencies of the SV, L, and SH modes, respectively, at $\bar{K}$ in the surface Brillouin zone.