Reversed anisotropies and thermal contraction of fcc (110) surfaces

Shobhana Narasimhan

Theoretical Sciences Unit and Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research,
Jakkur PO, Bangalore 560 064, India

The observed anisotropies of surface vibrations for unreconstructed fcc metal (110) surfaces are often reversed from the ''common sense'' expectation; for example, atoms in the top layer have larger amplitudes of vibration in the surface plane than normal to it, and the amplitudes normal to the surface are larger for atoms in the second layer than those in the first layer. The source of these reversals is investigated by performing *ab initio* density functional theory calculations to obtain the surface force constant tensors for Ag(110), Cu(110), and Al(110). The most striking result is a large enhancement in the coupling between the first and third layers of the relaxed surface, which strongly reduces the amplitude of out-of-plane vibrations of atoms in the first layer; the relaxation of interlayer spacings is found to be crucial in order to observe these effects. This enhancement also provides a partial explanation for the thermal contraction of interlayer distances. It is shown that the enhancement in the coupling between the first and third layers, and the consequent anomalous features, can be rationalized by simple geometric arguments.

I. INTRODUCTION

The low-index surfaces of face-centered cubic (fcc) metals are arguably the most studied of surfaces. Though they are often intended to serve as prototypes for understanding the behavior of more complex surface systems, it has become evident in the past two decades that even these ''simple'' surfaces display a wide range of complicated and often counterintuitive phenomena. In this paper, I consider the case of unreconstructed fcc (110) surfaces. I try to show that some of the observed features of their thermal behavior that have generally been accepted as violating ''common sense'' can actually be explained by simple arguments, backed up with results from *ab initio* density functional theory calculations. These results also have important implications for the study of other surface phenomena, and can, for example, provide insight into the mechanisms behind temperature-dependent surface phase transitions such as roughening and premelting.

More bonds are broken to create a (110) surface from a bulk fcc crystal, than for a (100) or (111) surface, and one therefore expects the departures from bulklike behavior to be largest for a (110) surface. Structurally, this is manifested in fcc metals in one of two ways: either the surface reconstructs into a ''missing row'' structure,[1] or the surface unit cell remains unchanged but there is a very pronounced oscillatory relaxation of interlayer spacings near the surface.[2] In either case, the very existence of the surface lowers symmetry, and one expects to find anisotropic modifications in the thermal properties of atoms at or near the surface.

The surprise is that for these unreconstructed fcc(110) surfaces, some of these anisotropies are *reversed*, i.e., they violate the ''common sense'' expectation. For example, experiments show that in general (i) atoms in the topmost surface layer have a bigger mean-squared displacement (MSD) in the surface plane than normal to it, whereas one might have expected the latter to be larger, since along this direction, there are no higher layers to repel the atoms in the first layer;[3,4] (ii) the MSD's normal to the surface are larger for second layer atoms than for first layer atoms, though one would expect that the MSD's should decay monotonically into the bulk;[5] (iii) a third curious fact about unreconstructed fcc (110) surfaces is that in some cases there is a thermal *contraction* of interlayer distances upon heating. The rule of thumb seems to be that if the first interlayer spacing d_{12} expands upon heating, then the next interlayer spacing d_{23} contracts;[3] however, if d_{12} exhibits a thermal contraction, then d_{23} expands with increasing temperature.[5,6]

Some of these patterns of behavior have also been observed in molecular dynamics (MD) simulations[7–9] but their origin remains a puzzle. In order to gain physical insight, and to be able to predict trends across differently oriented surfaces and different elements, one would like to not only reproduce this behavior in a theoretical calculation, but also to know where these anomalous properties arise from. Are they primarily a consequence of the bond topology, or are they due to peculiarities in the electronic structure? Such questions can reliably be answered by breaking up the process of obtaining a fully relaxed surface from the cleavage of a bulk crystal into steps, and performing a sequence of *ab initio* calculations at each component step.

There have been few *ab initio* calculations of the lattice dynamics and thermal behavior of the (110) surfaces of fcc metals. Most of the previous calculations have been empirical (involving *ad hoc* modifications of near-surface interactions so as to reproduce experimental phonon spectra),[10–13] or semiempirical.[7,8] The problem is, of course, that this procedure is not guaranteed to give a unique result, and one may be fooled into making modifications that are actually very far from the correct ones. The only fcc(110) surface that has been investigated in detail, using first-principles methods, is the Al(110) surface. The pioneering calculations of Ho and Bohnen[14] and other researchers[15,16] of the lattice dynamics of Al(110) have recently been followed by an impressive *ab initio* MD study,[9] which reproduces the experimentally observed anisotropies and the thermal contraction of d_{12}. But

can the behavior of a simple metal like Al also serve as an adequate paradigm for transition or noble metals? Computational constraints make it currently unfeasible to perform such *ab initio* MD simulations on the noble metals or on transition metals.

However, *ab initio* investigations of vibrational properties using the ''frozen phonon'' approach are possible, and have in fact been performed by previous authors on other low-index surfaces of these materials.[17] This is the approach followed in the present paper.

II. METHOD

In this paper, I present the results of a series of *ab initio* density functional theory calculations on the bulk fcc structures as well as the unreconstructed (110) surfaces of Ag, Cu, and Al. These calculations were performed using the package ''fhi96md,''[18] with fully separable norm-conserving pseudopotentials[19] and the Ceperley-Alder form of the local density approximation.[20] The calculations were carried out using plane wave basis sets with energy cutoffs of 60 Ry, 70 Ry, and 20 Ry for Ag, Cu, and Al, respectively. It has been verified in earlier studies that the pseudopotentials and basis sets used here work well for both bulk and surface properties of these metals.[21] The surface calculations for Ag and Cu were carried out using a repeating slab geometry comprised of seven layers of atoms, separated by a vacuum thickness equivalent to five layers; while a 15-layer slab was used for the calculations on Al(110).

First, the relaxed structures (lattice constant and interlayer spacings) were determined by minimizing the total energy and the Hellman-Feynman forces[22] on the atoms. Then, frozen-phonon calculations were performed to determine the exact interlayer and/or intralayer force constants from first principles, by distorting the equilibrium structure and computing the forces thereby induced on the atoms. For each type of distortion, the forces were computed for at least five values of displacements away from equilibrium, so as to ensure accurate determination of the force constants (first derivatives of forces with respect to displacements). Frozen-phonon calculations for the bulk structures were carried out using both the conventional cubic unit cell and a unit cell containing 12 to 16 layers of atoms stacked along the [110] direction. While performing frozen-phonon calculations on the surface structures, distortions and relaxations were confined to one side of the slab. As described below, frozen-phonon calculations on the surface structures were carried out on both the bulk-truncated (unrelaxed) slabs and the relaxed slabs (with interlayer spacings relaxed to the optimum values). Both interlayer and intralayer surface force constants were obtained in this way.

After determining the *ab initio* force constant tensors, these results were used to parametrize an interatomic potential, with separate parametrizations for the bulk and the surface. This parametrized form of the potential was then used to determine phonon eigenvalues and eigenvectors by setting up and diagonalizing a dynamical matrix. These in turn can be used to determine the atomic MSD's, as described in greater detail below. For each surface, this calculation was performed for three cases: (i) Neither electronic nor geometric relaxation was permitted, i.e., bulk coupling constants were used to calculate the MSD's for the surface atoms. (ii) Electronic relaxation was permitted, but not geometric relaxation, i.e., the interatomic potential was fit to the *ab initio* results for the force constants for the bulk-truncated surface, with all interlayer spacings unchanged from the bulk interlayer spacing d_B. (iii) Both geometric and electronic relaxation was permitted, i.e., the force constants determined for the fully relaxed surfaces were used. The advantage of carrying out the calculation in these three steps is that it enables one to pinpoint exactly what is responsible for the observed anomalous behavior. For example, one can get a handle on the relative importance of the bond topology (i.e., coordination number at the surface, and which atoms are bonded to each other) and the ways in which the surface force constants are modified as a result of changes in the electronic structure due to (a) cleavage and (b) relaxation.

III. RESULTS

A. Equilibrium structures

For all three elements, the bulk lattice constants a_0 determined from the *ab initio* calculations are in good agreement with experiments. For Ag, Cu, and Al, I obtain $a_0 = 4.06$ (4.09), 3.54 (3.61), and 3.94 (4.05) Å, respectively (the experimental values at room temperature are given in parentheses). Upon allowing interlayer spacings to relax, all three (110) surfaces display the pattern of damped oscillatory relaxation that is well known to be characteristic of these fcc(110) surfaces,[2] with alternating contractions and expansions of successive interlayer spacings. The changes with respect to the bulk interlayer spacing d_B of the first three interlayer spacings $\{d_{12}, d_{23}, d_{34}\}$ are $\{-6.9\%, +2.3\%, -1.2\%\}$, $\{-8.8\%, +3.8\%, -1.1\%\}$, and $\{-6.9\%. +3.5\%, -2.0\%\}$ for Ag, Cu, and Al, respectively.

B. Force constants

The interlayer force constants $\phi_{\alpha\beta}(i \ j)$ were obtained by moving the atoms in a layer i along the direction α, and computing the force along β then experienced by atoms in other layers j. For the case of bulk layers stacked along [110], I find that for all three materials, the only significant elements of the interlayer force constant tensors are the diagonal terms $\phi_{xx}(i, i\pm 1)$, $\phi_{yy}(i, i\pm 1)$, and $\phi_{zz}(i, i\pm 1)$ coupling nearest-neighbor layers, and $\phi_{zz}(i, i\pm 2)$ which couples next-nearest-neighbor layers (with the Cartesian directions defined as $\hat{x} = [1\bar{1}0]$, $\hat{y} = [001]$, and $\hat{z} = [110]$). All other elements of the interlayer force constant tensors are either zero by symmetry, or are smaller by at least an order of magnitude. Similarly, for the relaxed surfaces, the only significant terms involving the first (topmost) layer of atoms are $\phi_{xx}(1 \ 2)$, $\phi_{yy}(1 \ 2)$, $\phi_{zz}(1 \ 2)$, and $\phi_{zz}(1 \ 3)$.

Some of these results are presented in Fig. 1. For all three materials, I find that the elements of the interlayer force constant tensors stiffen considerably upon going from the bulk to the relaxed surface. The most notable feature is a dramatic increase in $\phi_{zz}(1 \ 3)$, whose magnitude is almost doubled
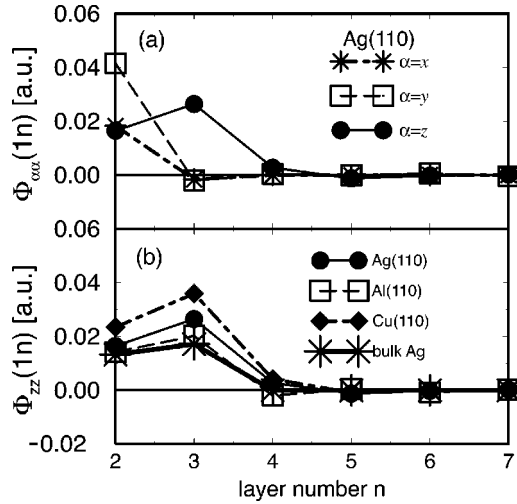
FIG. 1. Results from *ab initio* calculations for selected diagonal elements of the interlayer force constant tensors coupling the first layer of atoms with subsurface layers n, for the fully relaxed (110) surfaces of (a) Ag: xx, yy, and zz elements and (b) Ag, Al, and Cu: zz elements. The zz elements for bulk Ag are also shown. Note the very large value of $\phi_{zz}(1\ 3)$ for all three relaxed surfaces; it is argued in this paper that this is largely responsible for the anomalous thermal behavior of these surfaces.

relative to the bulk value $\phi_{zz}(i,i\pm2)$. In fact, $\phi_{zz}(1\ 3)$ is found to be significantly larger than $\phi_{zz}(1\ 2)$. This means that if the atoms in layer 1 are displaced along the z direction (normal to the surface) the resulting force along z experienced by atoms in layer 3 is considerably greater than the force on atoms in layer 2, which is a surprising and counterintuitive result. Though the result $\phi_{zz}(1\ 3)>\phi_{zz}(1\ 2)$ was also obtained by some previous authors who fit force constant models to empirical data for Al(110) (Ref. 11) and Ni(110),[23] its importance seems to have been overlooked. I will argue that this large enhancement in $\phi_{zz}(1\ 3)$ is largely responsible for the anomalous thermal behavior of these surfaces. In particular, it reduces the amplitude of vibration along z of atoms in the topmost layer (which would otherwise be large due to the reduced coordination at the surface), and damps the thermal expansion of d_{13}.

In this way, I have assembled an extremely large database of results from *ab initio* frozen-phonon calculations. In addition to the terms listed above, the database includes results for other interlayer force constants, as well as intralayer terms. It should be emphasized that the results I have obtained for force constant tensors are exact, and do not involve any assumptions about the form or range of interatomic potentials. However, I will now map these results onto a model potential, in order to better understand the implications of the changes in the surface force constant tensors.

C. Interatomic potentials and atomic mean squared displacements

The large database of *ab initio* results for force constant tensors is used to parametrize a simple form of interatomic
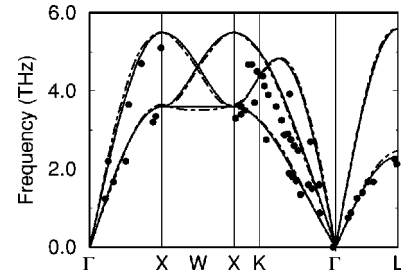

FIG. 2. Bulk phonon dispersion relation for fcc Ag. The solid lines are obtained from the two-parameter model described in this paper; the dot-dashed lines are from the *ab initio* linear response calculation of Xie *et al.* (Ref. 24), and the filled circles are data from neutron-scattering experiments (Ref. 28). The close agreement between the solid and dot-dashed curves suggests that the interatomic interactions for bulk Ag are well represented by nearest-neighbor pair potentials.

potential: for each pair of nearest-neighbor (NN) atoms the interatomic potential $U(r)$ is specified by a tangential parameter $\alpha=r_0^{-1}[dU(r)/dr]_{r=r_0}$ and a radial parameter $\beta=[d^2U(r)/dr^2]_{r=r_0}$, where r_0 is the equilibrium value of the interatomic distance r.

For the interaction between two NN atoms in the bulk, I obtain $\{\alpha_{bb},\beta_{bb}\}=\{-0.0007,0.0181\},\{-0.0006,0.0236\}$, and $\{-0.0007,0.0152\}$ for Ag, Cu, and Al, respectively, with all force constants being expressed in atomic units (Ha/bohr^2). The oscillatory relaxation and charge redistribution at the relaxed surfaces result in a modification of these values for bonds near the surface. Accordingly, four kinds of NN bonds i-j between atoms in near-surface layers i and j (1-1, 1-2, 1-3, and 2-3), are described by new parameters α_{ij} and β_{ij}, while all other terms are left unchanged from the bulk values.

Though this form of potential is admittedly simple, it gives bulk phonon spectra that are in good agreement with experiments as well as earlier *ab initio* calculations, and also suffices to bring out the essential physics behind the altered surface behavior. Figure 2 shows the phonon dispersion along high-symmetry directions for bulk Ag, as obtained from the parametrized form used in this paper (with the two parameters $\{\alpha_{bb}$ and $\beta_{bb}\}$ being fit to *ab initio* calculations). For comparison, the results from an earlier *ab initio* linear response calculation by Xie *et al.*[24] are also plotted; these latter calculations do not involve any parametrization of interatomic potentials. The agreement between my parametrized form and the *ab initio* linear response results is remarkably (and, in fact, surprisingly) good, and provides strong evidence for the adequacy of the parametrization used.

Moreover, though the parameter set is heavily overdetermined (with the eight modified surface parameters being fit to a database of 34 different numbers determined from *ab initio* calculations for 13 different kinds of surface distortions, supplemented by three stability criteria), the quality of the fit is good for Al, and excellent for Ag and Cu.

Next, the model potential is used to set up the dynamical matrix for a slab composed of many layers N stacked along

TABLE I. Comparison of calculated and experimental MSD's for atoms in the two topmost layers. T is the temperature in kelvin. Note the presence of the reversed anisotropies $\langle u_{1y}^2 \rangle > \langle u_{1z}^2 \rangle$ and $\langle u_{2z}^2 \rangle > \langle u_{1z}^2 \rangle$.

Material	Method	T (K)	$\langle u_{1x}^2 \rangle$	$\langle u_{1y}^2 \rangle$	$\langle u_{1z}^2 \rangle$	$\langle u_{2x}^2 \rangle$	$\langle u_{2y}^2 \rangle$	$\langle u_{2z}^2 \rangle$
Al(110)	this work	400	0.018	0.027	0.022	0.015	0.014	0.032
	AI-MD[a]	400		0.028	0.019		0.013	0.030
	LEED[b]	400			0.032			0.030
	MEIS[c]	330	0.020	0.027	0.018	0.012	0.015	0.015
Ag(110)	this work	300	0.013	0.021	0.014	0.010	0.010	0.026
	EAM[d]	300	0.014	0.020	0.013			
	MEIS[e]	300	0.022	0.048	0.026	0.012	0.022	0.026
Cu(110)	this work	300	0.008	0.009	0.010	0.006	0.007	0.010
	EAM[d]	300	0.011	0.019	0.013	0.008	0.010	0.014
	HAS[f]	300			0.012			

[a]Reference 9.
[b]Reference 6.
[c]Reference 4.
[d]Reference 7.
[e]Reference 3.
[f]Reference 27.

[110], which is then diagonalized to obtain phonon frequencies $\omega_{\mathbf{k}\lambda}$ and eigenvectors $e_{i\alpha}^{\mathbf{k}\lambda}$. The αth component of the MSD's at temperature T for atoms in layer i, $\langle u_{i\alpha}^2(T) \rangle$, is then given by[25]

$$\langle u_{i\alpha}^2(T) \rangle = \frac{1}{N}\sum_{\mathbf{k}\lambda} \frac{\hbar}{M\omega_{\mathbf{k}\lambda}}|e_{i\alpha}^{\mathbf{k}\lambda}|^2(n_{\mathbf{k}\lambda}+\tfrac{1}{2}), \qquad (1)$$

where the summation runs over all wave vectors $\mathbf{k}$ in the surface Brillouin zone and all phonon branches λ; $\hbar$ is Planck's constant, M is the atomic mass, and $n_{\mathbf{k}\lambda}$ is the Bose-Einstein distribution factor.

The geometry of the surface contributes to the MSD's both directly (via the coordination number) and indirectly (via the coupling constants, which depend on the electronic structure, which in turn depends on the geometry). A significant advantage of the present approach (relative to experiments or MD simulations) is that it enables one to easily and reliably disentangle the purely geometric effects from electronic ones. To do this, for each material I consider various cases. First, to determine the consequences of the reduced coordination at the surface *alone*, all NN interactions are replaced by the bulk parameters α_{bb} and β_{bb}. Upon using Eq. (1), I find that all components of the MSD's of atoms in the first two layers are larger than the corresponding bulk values, but the anisotropies differ from those seen in experiments and MD simulations: the largest enhancement is in $\langle u_{1y}^2 \rangle$ and $\langle u_{1z}^2 \rangle$, which are both approximately 2.2 times as large as in the bulk, and $\langle u_{1z}^2 \rangle > \langle u_{2z}^2 \rangle$. Hitherto, there has been a tendency to attribute any anomalies in the behavior of fcc(110) surfaces to the "very open" surface structure. However, these results show that the open structure *alone* is not sufficient to explain the observed phenomena.

The situation is considerably altered for the three relaxed surfaces. The changes in the surface force constant tensors

result in a considerable increase (15 to 50 %) in the value of the radial term β_{12}, and an even larger increase (45 to 85 %) in β_{13}, relative to β_{bb}. The huge enhancement in β_{13} corresponds to the very large value obtained for $\phi_{zz}(1\ 3)$, and implies that the bonds between NN atoms in layers 1 and 3 are extremely stiff. However, I find that the radial term coupling two NN surface atoms, β_{11}, is softened by ~20%. These results differ considerably from the 40% softening suggested for β_{11} for Ag(110) by Franchini *et al.*,[13] and the softening of β_{12} by 6% for Cu(110) suggested by Black *et al.*,[12] who fit the parameters of their models to experimentally measured phonon spectra.

What is responsible for the increased stiffness of the 1–3 NN bonds? To answer this, I looked also at the intermediate case of bulk-truncated surfaces (with electronic relaxation permitted, but all interlayer distances set equal to the bulk value). I find that though the value of β_{13} relative to β_{bb} is slightly modified for the bulk-truncated surfaces, the huge enhancement comes upon going from the bulk-truncated surface to the fully relaxed one. The enhancement in β_{13} for the fully relaxed surfaces is sufficiently large to push $\langle u_{1z}^2 \rangle$ down significantly, now making $\langle u_{1z}^2 \rangle < \langle u_{2z}^2 \rangle$ and $\langle u_{1z}^2 \rangle < \langle u_{1y}^2 \rangle$.

Table I shows the results obtained for selected MSD's using the modified surface force constants and Eq. (1). These results compare well with those deduced from measurements using low-energy electron diffraction (LEED), medium energy ion scattering (MEIS), and helium atom scattering (HAS), as well as MD simulations using either *ab initio* (AI-MD) or embedded atom method (EAM) potentials (there is, however, a considerable scatter in the values of MSD's available in the literature). It is important to note that my results do not include anharmonic effects, which may be large for fcc (110) surfaces, especially Cu(110).[26] Thus any discrepancy between my results and the experimental or MD ones may indicate that anharmonic effects are significant.

D. Implications for thermal expansion

As discussed above, the large enhancement in β_{13} for the relaxed surfaces is largely responsible for the reversed anisotropies in the MSD's. Another consequence of the increased value of β_{13} is that the surface will try to always maintain a fixed value for the interlayer separation d_{13}, if necessary at the expense of changes in d_{12} and d_{23}. This tendency has been confirmed by additional calculations in which, upon varying d_{12}, d_{23} was found to change in such a way that d_{13} was approximately constant. One can now understand why, upon heating an unreconstructed fcc(110) surface, while d_{12} and d_{23} may expand/contract, they usually do so in such a way that d_{13} remains roughly constant, i.e., if one contracts the other expands. Of course a full treatment of the thermal expansion/contraction will require that one take into account the anharmonicity of the interatomic interactions. However, since the coefficient of thermal expansion in an anharmonic well depends on *both* the harmonic and anharmonic force constants, and is directly proportional to the cubic force constant but inversely proportional to the *square* of the harmonic force constant, the fact that β_{13} is considerably larger than β_{12} and β_{23} makes it likely that the thermal variation in d_{13} $(=d_{12}+d_{23})$ will be much less than the individual variations in d_{12} and d_{23} (assuming that the anharmonic coefficients do not differ widely).

To explain why, for example, d_{12} expands and d_{23} contracts upon heating Ag(110), whereas the reverse happens for Al(110), one has to go beyond the harmonic sector and examine the anharmonicity of the interlayer potentials. As for fcc(111) surfaces,[21] simple arguments based upon the anharmonicity of vibrations along z alone do not appear to suffice, nor does the vacuum appear to "act as a hard wall," as has been suggested for Al(110).[9]

Figures 3(a) and 3(b) show how the total energy of an Al(110) slab changes upon moving (a) the topmost and (b) the second layer of atoms by an amount z normal to the surface. Quartic polynomials of the form $E(z)=\frac{1}{2}\beta z^2+\gamma z^3+\delta z^4$ are fit to the *ab initio* results, with positive z defined as an excursion towards the vacuum. For movement of the topmost layer, I obtain $\beta=0.0076$, $\gamma=-0.0079$ and $\delta=0.0030$ (all in atomic units); for shifts in the position of the second layer, I get $\beta=0.00815$, $\gamma=-0.0085$, and $\delta=0.0104$. Note that in both cases, γ is negative, i.e., the potential becomes steeper for displacements towards the bulk, rather than for displacements towards the vacuum, which is not what one would expect if the vacuum were indeed to act as a hard wall, as has been suggested[9] by Marzari *et al.* They have also suggested that the reason for the thermal contraction of d_{12} is that the anharmonicity along the z direction makes it easier for layer 2 to expand outwards than for layer 1. However, I find that the ratio $-\gamma/\beta^2$, which specifies the tendency for the layer to move outwards (thermal expansion), is 138 for the first layer, and 127 for the second layer, i.e., it is approximately the same for both layers, and in fact is slightly *greater* for the first layer. In other words, if one considers vibrations along the z direction alone, both layers 1 and 2 will move outwards upon heating the surface, and layer 1 will move slightly more than layer 2.
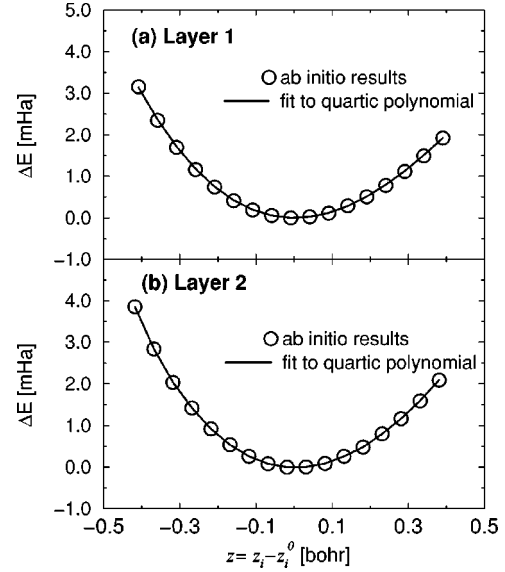

FIG. 3. Change ΔE in the total energy of an Al(110) slab upon moving (a) the topmost layer and (b) the second layer by an amount z normal to the surface. The circles are the results of *ab initio* calculations; the solid lines are fits to quartic polynomials. These curves give information about the anharmonicity of the vibrations, normal to the surface, of the first two atomic layers. Both curves become steeper upon moving towards the bulk rather than towards the vacuum, indicating a tendency for both layers to move outwards (due to these out-of-plane vibrations *alone*) upon heating. However, the vibrations of the two layers are coupled, and there are additional contributions from in-plane vibrations, as discussed in the text.

The actual situation is a complex scenario involving two additional complications: (i) One has to include the anharmonicity of both in-plane and out-of-plane vibrations, i.e., in addition to anharmonic terms of the form γz^3, one has to include terms such as $\gamma' x^2 z$, $\gamma'' xz^2$, etc. (ii) There is a coupling of the variables d_{12}, d_{23} and d_{13}. [This effect is particularly strong for fcc(110) surfaces, though it is negligible for fcc (111) and (100) surfaces.] It is possible to treat these effects within a quasiharmonic approximation, as has been done for other surfaces.[21,24] However, these considerations are beyond the scope of the present paper, where I have restricted myself to looking primarily at the significant implications that the physics at harmonic order has for the thermal behavior of these surfaces.

IV. DISCUSSION AND SUMMARY

The main result of the present paper is the seemingly counterintuitive one that for the relaxed (110) surfaces of Ag, Cu, and Al, there is a very large enhancement in $\phi_{zz}(1\ 3)$, an element of the force constant tensor that couples the *first* and *third* layers. This enhancement in $\phi_{zz}(1\ 3)$ (which, in the model interatomic potential used in this paper, maps onto a huge increase in the coupling constant β_{13}), is large enough to significantly reduce the amplitude of vibration of first-layer atoms along the z direction, thus reversing the expected anisotropies in MSD's, and damping the thermal expansion of d_{13}. In order to understand whether this result can
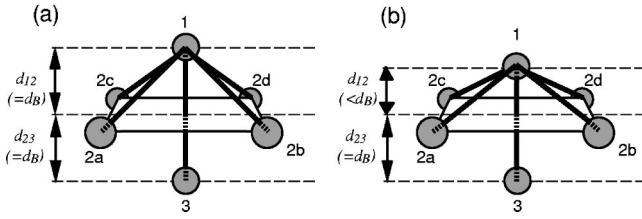
FIG. 4. These figures show the bond geometry for fcc(110) surfaces, and how the NN bond lengths change with the contraction of d_{12}. Atom 1 is in the topmost layer, atoms 2a, 2b, 2c, and 2d are in the second layer, and atom 3 is in the third layer. The thick black lines show the interlayer NN bonds involving atom 1. (a) For the bulk-truncated (unrelaxed) surface, the four 1-2 bonds, and the 1-3 bond all have the same length. (b) For the relaxed surface, the first interlayer spacing d_{12} is contracted, resulting in a shortening of all five bonds shown. However, the 1-3 bond is now shorter than the four 1-2 bonds. For clarity, the contraction of d_{12} is exaggerated in this figure; in reality, the contraction is about 7 to 10%. Also, the expansion of d_{23} is not shown in this figure for simplicity.

be generalized to other surfaces, we have to ask: Where does this enhancement come from?

The fact that all three materials display the same trends at harmonic order, and the large impact of allowing for the relaxation of interlayer spacings, suggest that the enhanced stiffening of β_{13} over all other β_{ij}'s may be more a consequence of the bonding geometry than of special features of the electronic structure. There are two relevant features in the geometry of fcc(110) surfaces: (i) A topological peculiarity of fcc(110) surfaces [but not the (111) or (100) surfaces] is that a surface atom is connected by NN bonds to atoms in the first, second *and third* layers of atoms parallel to the surface. [This explains why $\phi_{zz}(1\ 2)$ and $\phi_{zz}(1\ 3)$ may have comparable value, but not why the latter should be much larger.] (ii) There is a very large reduction in the coordination of surface atoms, as a result of which the bulk-truncated surface relaxes by decreasing d_{12} significantly.

The large enhancement in β_{13} and the smaller increase in β_{12} can be rationalized, *a posteriori*, by simple trigonometry. One has to realize that for the fcc(110) geometry, upon contraction of d_{12} (and thus also of d_{13}), the shortening of the interatomic bond lengths r_{12} and r_{13} does not scale uniformly with the contraction of the corresponding interlayer separations d_{12} and d_{13}. This is illustrated in Fig. 4, which shows schematically the interlayer bonds involving atoms in the first layer. The atom "1" in the topmost layer is connected by nearest-neighbor bonds to four atoms ("2a," "2b," "2c," and "2d") in the second layer, and to one atom ("3") that lies directly below it in the third layer. Figure 4(a) shows the

case of the bulk-truncated surface, with both d_{12} and d_{23} $=d_B$. In this case, the length of the bonds connecting the atom "1" to the four "2" atoms is the same as the length of the bond connecting "1" and "3." In Fig. 4(b), the topmost layer has moved downwards, so that now $d_{12}<d_B$. As a result, both the 1-2 bonds and the 1-3 bond have shortened; however the change in the former is less than the change in the latter. For example, a 10% contraction in d_{12}, relative to the bulk interlayer spacing d_B, translates to a 5% contraction in the NN bond length between atoms in layers 1 and 3, but a contraction of only 2.4% for the NN bond between atoms in layers 1 and 2. Since the stiffness of bonds scales inversely as a high power of their equilibrium length,[27] this results in a much larger increase in the radial force constant for 1-3 than 1-2 bonds.

The increase in d_{23} that results from the oscillatory relaxation of these surfaces weakens this effect. However, these simple geometric considerations suggest that if d_{23} is still small enough relative to d_B so that $d_{23}^2+2d_{12}d_{23}-3d_B^2<0$, one can still expect to find that $\beta_{13}\gg\beta_{12}$. Similarly, if the contraction of d_{34} is sufficiently small, then the radial force constant β_{24} should be softened, thus increasing $\langle u_{2z}^2\rangle$ further.

Another significant result of the present paper is that a simple model interatomic potential involving radial and tangential terms between nearest-neighbor atoms is found to work remarkably well for Ag, Cu, and Al, and gives results that are in excellent agreement with those from *ab initio* linear response calculations.

It has been shown above that Ag(110), Cu(110), and Al(110) show marked similarities in the behavior of their harmonic force constants, and given the simplicity of the geometric arguments, it should also be easy to extend these results to the unreconstructed (110) surfaces of other fcc metals. Thus, the reversed anisotropies and the very small thermal variation in d_{13}, which follow directly from the behavior of the harmonic force constants, may be expected to be general features of all such surfaces. It would, however, be interesting to check what happens for "true" transition metals with partially filled d shells, in which directional bonding effects may be more important. While more accurate calculations would need to fully incorporate the effects of anharmonicity, I hope to have shown that the physics at harmonic order can go a long way towards explaining some of the surprising thermal properties of these surfaces.

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