Reversed anisotropies and thermal contraction of FCC (110) surfaces

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Abstract

The observed anisotropies of surface vibrations for unreconstructed FCC metal (110) surfaces are often reversed from the “common sense” expectation. The source of these reversals is investigated by performing \textit{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. This also provides a simple explanation for the thermal contraction of interlayer distances. Both the anisotropies and the thermal contraction arise primarily as a result of the bond topology, with all three (110) surfaces showing similar behavior.
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 last two decades that even these “simple” surfaces display a wide range of complicated and often counter-intuitive 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 bulk-like 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]; (ii) the MSDs normal to the surface are larger for second layer atoms than for first layer atoms, though one would expect that the MSDs should decay monotonically into the bulk [4]; (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 \cite{3}; however, if $d_{12}$ exhibits a thermal contraction, then $d_{23}$ expands with increasing temperature \cite{3,4}.

Some of these patterns of behavior have also been observed in molecular dynamics (MD) simulations \cite{7,8} 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 \textit{ab initio} calculations at each component step.

There have been few \textit{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 \textit{ad hoc} modifications of near-surface interactions so as to reproduce experimental phonon spectra) \cite{10,11,12,13}, or semi-empirical \cite{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 \cite{14} and other researchers \cite{15,16} of the lattice dynamics of Al(110) have recently been followed by an \textit{ab initio} MD study \cite{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 \textit{ab initio} MD simulations on the noble metals or on transition metals.

However, \textit{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 \cite{17}. In this paper, I present the results of a series of such
frozen phonon calculations on the bulk FCC structures as well as the unreconstructed (110) surfaces of Ag, Cu and Al.

For each case, I have determined the exact interlayer and/or intralayer force constants from first principles, by distorting the equilibrium structure and computing the Hellman-Feynman forces [18] thereby induced on the atoms. These forces, as well as the relaxed structures, were obtained by performing density functional theory calculations using the package “fhi96md” [19], with fully separable norm-conserving pseudopotentials [20] and the Ceperley-Alder form of the local density approximation [21]. The calculations were carried out using plane wave basis sets with energy cut-offs 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 [22].

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). Bulk calculations 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.

The interlayer force constants \( \phi_{\alpha\beta}(i,j) \) were obtained by moving the atoms in a layer \( i \) along the direction \( \alpha \), and computing the force along \( \beta \) 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 \( \phi_{xx}(i,\pm 1) \), \( \phi_{yy}(i,\pm 1) \) and \( \phi_{zz}(i,\pm 1) \) coupling nearest-neighbor layers, and \( \phi_{zz}(i,i \pm 2) \) which couples next-nearest-neighbor layers (with the Cartesian directions defined as \( \hat{x} = [110], \hat{y} = [001] \) 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 Figure 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 relative to the bulk value $\phi_{zz}(i, i \pm 2)$. 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 counter-intuitive 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) \cite{11} and Ni(110) \cite{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.

It should be emphasized that the results I have obtained for interlayer force constant tensors are exact, and do not involve any assumptions about the form or range of interatomic potentials. However, I now map these results onto a model potential, in order to better understand the implications of the changes in the surface force constant tensors.

For each case, I have first assembled an extremely large database of results from \textit{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. This database is then used to parametrize a simple form of interatomic 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 $\{\alpha_{bb}, \beta_{bb}\} = \{-0.007, 0.181\}, \{-0.006, 0.0236\}$ and $\{-0.007, 0.0152\}$ 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. 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 $\alpha_{ij}$ and $\beta_{ij}$, while all other terms are left unchanged from the bulk values.
Though this form of potential is admittedly simple, it is able to reproduce the gross details of the bulk phonon spectrum, and suffices to bring out the essential physics behind the altered surface behavior. 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 \textit{ab initio} calculations for 13 different kinds of surface distortions, supplemented by three stability criteria), the quality of the fit is reasonable for Al, and extremely good 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 [110], which is then diagonalized to obtain phonon frequencies $\omega_{k\lambda}$ and eigenvectors $e_{i\alpha}^{k\lambda}$. The $\alpha$th component of the MSDs at temperature $T$ for atoms in layer $i$, $\langle u_{i\alpha}^2(T) \rangle$, is then given by [24]:

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

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

In order to disentangle geometric effects from electronic ones, for each material I consider various cases. First, to determine the consequences of the reduced co-ordination at the surface alone, all NN interactions are replaced by the bulk parameters $\alpha_{bb}$ and $\beta_{bb}$. Upon using Equation (1), I find that all components of the MSDs 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 $\langle u_{1x}^2 \rangle > \langle u_{2x}^2 \rangle$. 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 $\beta_{12}$, and an even larger increase (45 to 85%) in $\beta_{13}$, relative to $\beta_{bb}$. The huge enhancement in $\beta_{13}$ 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, $\beta_{11}$, is softened by $\sim 20\%$. These results differ considerably from the 40\% softening suggested for $\beta_{11}$ for Ag(110) by Franchini et al. \cite{13}, and the softening of $\beta_{12}$ by 6\% for Cu(110) suggested by Black et al. \cite{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 $\beta_{13}$ relative to $\beta_{bb}$ 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 $\beta_{13}$ 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 $\langle u_{1z}^2 \rangle < \langle u_{1y}^2 \rangle$. Thus, it is not that “the vacuum acts as a hard wall”, as has been suggested as an explanation for the reversed anisotropies on Al(110) \cite{9}, but the sub-surface atoms that constitute the hard wall that damps the vibrations along $z$ of atoms in the surface layer.

Another consequence of the increased value of $\beta_{13}$ 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 is inversely proportional to the square of the harmonic force constant, the stiffening of $\beta_{13}$ can be expected to have a big impact on the thermal variation of $d_{13}$.  

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The fact that all three materials display the same trends, and the large impact of allowing for the relaxation of interlayer spacings, suggest that the enhanced stiffening of $\beta_{13}$ over all other $\beta_{ij}$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) there is a very large reduction in the co-ordination of surface atoms, as a result of which the bulk-truncated surface relaxes by decreasing $d_{12}$ significantly, (ii) 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.

However, the large enhancement in $\beta_{13}$ and the smaller increase in $\beta_{12}$ 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 $d_{13}$. 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 as a high power of their equilibrium length, 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 $\beta_{24}$ should be softened, thus increasing $\langle u_{2z}^2 \rangle$ further.

Table I shows the results obtained for selected MSDs using the modified surface force constants and Equation 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 \textit{ab initio} (AI-MD) or Embedded Atom Method (EAM) potentials (there is, however, a considerable scatter in the values of MSDs 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) \cite{26}. Thus any discrepancy between my results and the experimental or MD ones may indicate that anharmonic effects are significant.

The calculations presented in this paper can be extended by including anharmonic interactions within a quasiharmonic approximation, as has been done for other surfaces \cite{22,27}. However, I hope to have shown that the physics of the harmonic sector is itself interesting, and can go a long way towards predicting and understanding the thermal behavior of FCC(110) surfaces. 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.
REFERENCES

[1] M. Copel and T. Gustafsson, Phys. Rev. Lett. 57, 723, and references therein.

[2] R.N. Barnett et al., Phys. Rev. B 27, 6534 (1983).

[3] B.W. Busch and T. Gustafsson, Surf. Sci. 407, 7 (1998).

[4] B.W. Busch and T. Gustafsson, Phys. Rev. B 61, 16097 (2000).

[5] A. Mikkelsen, J. Jiruse and D.L. Adams, Phys. Rev. B 60, 7796 (1999).

[6] H. Goebel and P. von Blanckenhagen, Phys. Rev. B 47, 2378 (1993).

[7] L. Yang and T.S. Rahman, Phys. Rev. Lett. 67 2327 (1991); T.S. Rahman and Z.J. Tian, Journ. of Elec. Spect. and Relat. Phenom. 64/65, 651 (1993).

[8] Y. Beaudet, L.J. Lewis and M. Persson, Phys. Rev. B 50 12084 (1994); H. Hakkinen and M. Manninen, Phys. Rev. B 46, 1725 (1992).

[9] N. Marzari et al. Phys. Rev. Lett. 82, 3296 (1999).

[10] J.A. Stroscio et al. Phys. Rev. Lett. 54, 1428 (1985).

[11] M. Persson, J.S. Stroscio and W. Ho, J. Electron. Spectrosc. Relat. Phenom. 38, 11 (1986).

[12] J.E. Black et al. Phys. Rev. B 36 2996 (1987).

[13] A. Franchini et al., Phys. Rev. B 38, 12139 (1988).

[14] K.M. Ho and K.P. Bohnen, Phys. Rev. Lett. 56, 934 (1986).

[15] J.A. Gaspar et al. Phys. Rev. Lett. 66, 337 (1991).

[16] A. Franchini et al., Phys. Rev. B 47, 4691 (1993).

[17] Y. Chen et al., Phys. Rev. Lett. 70, 603 (1993); S.Y. Tong et al., Surf. Rev. and Lett. 1, 97 (1994).
[18] H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Liepzig, 1937); R.P. Feynman, Phys. Rev **56**, 340 (1939).

[19] M. Bockstedte *et al.*, Comp. Phys. Comm. **107**, 187 (1997).

[20] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).

[21] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[22] S. Narasimhan and M. Scheffler, Z. Phys. Chem. **202**, 253 (1997); S. Narasimhan, Surf. Sci. Lett. **417**, L1166 (1998).

[23] S. Lehwald *et al.*, Surf. Sci. **131**, (1987).

[24] R.E. Allen and F.W. de Wette, Phys. Rev. **179**, 873 (1969).

[25] P. Zeppenfeld, Ph.D. Thesis, KFA Jülich (1989).

[26] P. Zeppenfeld *et al.*, Phys. Rev. Lett. **62**, 63 (1989); G. Armand and P. Zeppenfeld, Phys. Rev. B **40**, 5936 (1989); A.P. Baddorf and E.W. Plummer, Phys. Rev. Lett. **66**, 2770 (1991); A.M. Raphuthi *et al.*, Phys. Rev. B **52**, R5554 (1995).

[27] J. Xie *et al.*, Phys. Rev. B **59**, 970 (1999).
FIGURES

FIG. 1. Results from \textit{ab initio} calculations for selected diagonal elements of the interlayer force constant tensors coupling the first layer of atoms with sub-surface layers $n$, for the fully relaxed (110) surfaces of (a) Ag: $xx$, $yy$ and $zz$ elements (b) Ag, Al and Cu: $zz$ elements. The $zz$ elements for bulk Ag are also shown.
TABLE I. Comparison of calculated and experimental MSDs for atoms in the two topmost layers. $T$ is the temperature in Kelvin, and $\langle u^2_{bi} \rangle$ is the one-dimensional MSD of bulk atoms.

| Material   | Method   | $T$(K) | $\langle u^2_{1x} \rangle$ | $\langle u^2_{1y} \rangle$ | $\langle u^2_{1z} \rangle$ | $\langle u^2_{2x} \rangle$ | $\langle u^2_{2y} \rangle$ | $\langle u^2_{2z} \rangle$ |
|------------|----------|--------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Al(110)    | this work| 400    | 0.018                    | 0.027                    | 0.022                    | 0.015                    | 0.014                    | 0.032                    |
| Al-MD\textsuperscript{a} | 400 | 0.028 | 0.019 | 0.013 | 0.030 |
| LEED\textsuperscript{b} | 400 | 0.032 |                 |                  | 0.030 |                  |
| MEIS\textsuperscript{c} | 330 | 1.5$\langle u^2_{bi} \rangle$ | 1.2$\langle u^2_{bi} \rangle$ | 1.1$\langle u^2_{bi} \rangle$ | |
| Ag(110)    | this work| 300    | 0.013                    | 0.021                    | 0.014                    | 0.010                    | 0.010                    | 0.026                    |
| EAM\textsuperscript{d} | 300 | 0.014 | 0.020 | 0.013 | | |
| MEIS\textsuperscript{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\textsuperscript{d} | 300 | 0.011 | 0.019 | 0.013 | 0.008 | 0.010 | 0.014 | |
| HAS\textsuperscript{f} | 300 |                  |                  |                  |                  |                  | 0.012 | | |

\textsuperscript{a}Ref. 9
\textsuperscript{b}Ref. 6
\textsuperscript{c}Ref. 4
\textsuperscript{d}Ref. 7
\textsuperscript{e}Ref. 3
\textsuperscript{f}Ref. 25
(Narasimhan, Fig. 1)

(a) $\Phi_{\alpha \alpha}(1n)$ [a.u.]

(b) $\Phi_{zz}(1n)$ [a.u.]