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Shear Horizontal Vibrations at the (0001) Surface of Beryllium

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We report the results of a high-resolution Electron-Energy Loss Spectroscopy (EELS) investigation of Be(0001) surface. Two dispersive surface vibrational modes are observed in the Γ to $\bar{M}$ direction: a sagittal-plane mode (the Rayleigh wave) and a shear horizontal mode. We have compared our experimental results to a 300-layer slab calculation and to a semi-infinite Green's function calculation of Sameth and Mele. Compared with the experimental results, both calculations predict a higher energy for the Rayleigh wave and lower energy for the shear horizontal mode. These results are consistent with stronger in-plane bonding and weaker interplanar bonding at the surface, in accord with other theoretical predictions.

It is well known that the properties of metal surfaces can be quite different from those of the bulk. The differences arise, ultimately, from the fact that surface atoms reside in sites of lower coordination, and have fewer neighbors, than atoms in the bulk. The loss of neighbors at the surface can have effects on the bonding which lead, for example, to surface relaxation. For metals where there is a large degree of localized bonding, i.e. transition- and noble-metals, the loss of coordination can lead to surface reconstruction. Much of our knowledge about bonding at surfaces is derived from measurements of surface structure. For example, first-principles calculations have shown that the stability of a missing-row reconstruction at the (110) surfaces of Au and Ag is related to the competition between d-d bonding and the associated compression of s-p electrons [1].

The surface structure of s-p bonded metals has been assumed to be "simple" in the sense that in the absence of directional or localized bonding, interaction with the ion core can be regarded as a perturbation to an

otherwise homogeneous system. In many ways, these systems are realizations of the "jellium" model in which the surface physics can be parameterized in terms of the electron density. The physical properties of free-electron metals are determined mainly by properties of the electron gas. For instance, recent theoretical work shows convincingly that the proper treatment of screening in the surface region is required in order to quantitatively explain the surface relaxation of simple-metal surfaces [2].

Although s-p bonded, beryllium does not easily fit into the common picture of an s-p bonded metal. One clear indication is that in contrast to the free-electron picture beryllium exhibits a *minimum* in the bulk density of states at the fermi level. Deviation from the free-electron picture is also evident in the surface structure of Be; low-energy electron diffraction (LEED) studies indicate that the first interplanar spacing at the (0001) surface is expanded by almost 6% [3]. The Be(11 $\bar{2}$ 0) surface exhibits a missing-row reconstruction similar to that observed at the fcc(110) surfaces, where localized bonding (d-d) has been shown to be important in the mechanism of reconstruction [4]. These anomalous properties may be related to the

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mechanism of bonding in bulk beryllium; Be has an atomic configuration of completely filled shells ($1s^2 2s^2$). Bonding in the bulk is achieved via hybridization of the 2s electrons with the unoccupied 2p levels. This hybridization is possible because the 2p-levels experience a dramatic energy lowering in the bulk environment due to overlap with the s-cores of neighboring atoms. The degree of hybridization is sensitive to the local atomic geometry. For instance, the occupied p bandwidth of an isolated Be monolayer is only 20% of the occupied s bandwidth while in bulk Be it is nearly 40% [5]. Reduction of s-p hybridization may also be responsible for the structure of Be surfaces. A recent first-principles calculation attributes the first-layer expansion of Be(0001) to a weakening of the interplanar bonding, which is a consequence of the reduction of s-p hybridization at the surface [6]. Similar conclusions have also been drawn for the Be dilayer [7].

Surface vibrations offer a way of probing dynamical aspects of surface bonding. The displacements of the ion cores leads to an adiabatic rearrangement of the surrounding valence charge. The screening properties of the valence charge contribute to the energy associated with the vibrational mode, and may be quite sensitive to the degree of hybridization at the surface. Chulkov [8] has pointed out that the existence of surface states at the Be(0001) surface leads to an increase in the surface electronic density of states near the fermi energy. This increase could dramatically alter the screening, quite apart from the anisotropy induced by the truncation of the bulk. Screening effects have been shown to be important in the understanding anomalous features in the dispersion of vibrational modes at the Al(100) surface [9].

We have measured the dispersion of vibrational modes at the Be(0001) surface

with EELS in order to understand the influence of surface electronic structure on the surface dynamics. The measurements have centered on the $\bar{M}$ point in the surface Brillouin zone because this point is accessible in two different scattering geometries, $\bar{\Gamma}$ to $\bar{M}$, and $\bar{\Gamma}$ to $\bar{K}$; When scattering along the $\bar{\Gamma}$ to $\bar{M}$ direction, the sagittal plane coincides with mirror plane of the hcp crystal structure. The geometry of the (0001) surface is shown in Fig. 1.

Figure 1. Geometry of the hcp(0001) surface in reciprocal and real space. Open circles represent top-layer atoms. Shaded circles represent second-layer atoms. One of three equivalent mirror planes is shown.

Two surface vibrational modes have been measured at $\bar{M}$, the Rayleigh Wave (RW), for which the atomic displacements are normal to the surface, and a shear horizontal (SH) mode, with atomic displacements parallel to the surface. Slab calculations indicate that both modes are localized almost

entirely in the top surface layer (95% for RW, 85% for SH). However, force constants derived from a fit to the bulk phonon spectra do not predict the correct energies for the surface modes: the calculated RW energy is *higher* and the SH mode energy is *lower*. The observation of SH modes is particularly illuminating since these modes are most sensitive to in-plane forces, and offer an important test of theories developed primarily to explain sagittal-plane modes. Unfortunately, only a few experimental investigations of SH modes have been reported in the literature [9.2].

A Be(0001) sample was cut and polished using procedures described elsewhere [4]. The sample was attached to a manipulator capable of azimuthal rotation and tilt. A clean surface was prepared in UHV by repeated cycles of sputtering with 1.0 keV Ne ions at a sample temperature of 450°C. Sputtering at elevated temperatures was necessary to remove residual amounts of adsorbed oxygen. Each sputtering cycle was followed by an annealing period at 450°C. Adsorption of contaminants was monitored with EELS. LEED was used to align the scattering plane to the desired crystal direction. Phonon spectra were recorded in an incident energy range of 20-150 eV, at a resolution of 3-4 meV. The incident and scattered angles were chosen such that $\theta_i + \theta_s \approx 90^\circ$. All spectra were recorded at room temperature.

EELS spectra sampling the $\bar{M}$ point in the surface Brillouin zone are illustrated in Fig. 2. The top spectrum was obtained with the scattering plane aligned parallel to the $\bar{\Gamma}$ to $\bar{M}$ direction. Only one feature is observed: the Rayleigh wave at an energy of 39.5 meV. No other features are observed in the range of impact energies investigated. The lower spectrum was recorded with the scattering plane rotated parallel to the $\bar{\Gamma}$ to $\bar{K}$ direction. An additional feature, at 50.5 meV, is observed at $\bar{M}$. This feature is located at the

edge of the surface-projected bulk bands, and is significantly broader than the RW. The initial and final electron states in an EELS experiment are even under reflection in the sagittal plane; if the displacement pattern of this mode is completely odd under reflection in the mirror plane, the mode will not be excited when the sagittal plane and mirror plane coincide [9.5].

Figure 2. (a) spectrum recorded at 50 eV at $\bar{M}$ with sagittal plane aligned parallel to the $\bar{\Gamma}$ to $\bar{M}$ direction, and (b) spectrum recorded at 85 eV at $\bar{M}$ with the sagittal plane aligned parallel to the $\bar{\Gamma}$ to $\bar{K}$ direction.

A series of spectra were recorded with the sample in a slightly tilted and rotated geometry. Inspection of the LEED pattern indicated that the sagittal plane was tilted by 1.5° from the sample normal, and was rotated 4° from the $\bar{\Gamma}$ to $\bar{M}$ direction. EELS spectra

recorded for this scattering geometry are shown in Fig. 3.

Figure 3. A series of spectra obtained for 50 eV incident energy for momentum transfer along the $\bar{\Gamma}$ to $\bar{M}$ direction. The scattering geometry is described in the text.

The mode at 50.5 meV is clearly visible in the slightly-tilted and rotated geometry but is not observed when the sagittal plane is carefully aligned. Furthermore, this mode disperses in a manner which suggests it is coupled to the projected bulk bands.

In an effort to identify the observed features we have compared our results to the predictions of two models of the Be(0001) surface: a 300-layer slab calculation based on central forces, and a semi-infinite Green's function calculation of Sameth and Mele, which includes general tensor-force couplings between atoms. Both calculations

were performed for a bulk-terminated surface with parameters determined from bulk phonon data [9.7]. These two methods are somewhat complementary; the density of states which is extracted from the more general Green's function method serves as a check on the computed slab density of states, whereas eigenvectors and empirical "force constants" are more easily obtained from the slab calculation.

The results of slab calculations based on central forces must be viewed with some caution. For many metals it is possible to adequately fit bulk phonon data by assuming that each atom is located at the minima of the pair potentials connecting shells of neighbors [9.8]; that is, the derivative of the pair potential connecting n th-nearest neighbors, ϕ'_n , is zero when evaluated at the equilibrium atomic positions. Stability conditions based on the first derivative of the pair potentials [9.9] are therefore identically satisfied and the resulting slab is guaranteed to be in equilibrium, and to give the correct bulk lattice constants. However, for some materials, and especially those for which three-body forces are important [10], central-force models are incapable of reproducing some bulk features, even with non-zero values for ϕ'_n . Unfortunately, this is the case for Be [11]; We find that models including up to eighth-nearest neighbors, with ϕ'_n equal to zero, do not give a very good description of the bulk lattice dynamics. A much better fit results from a model including third-nearest neighbors and unrestricted values for the ϕ'_n . We have chosen a model which includes third-nearest neighbor interactions, with non-zero values for ϕ'_n . Imposing equilibrium conditions to ensure a "stress free" slab leads to relations among the ϕ'_n which must be satisfied globally [9.9]. The resulting model contains four free parameters. Satisfying the equilibrium conditions for the slab requires well-defined adjustments of the surface ϕ'_n .

For the present model, *compressive* surface stress arising from non-zero ϕ 's in the bulk is eliminated if the value of ϕ for second-nearest neighbors of surface atoms is reduced by a factor of 2. That is, bulk force constants applied to surface atoms, with no adjustment, violate the global requirement that variation of the total energy with respect to the changes in the value of the in-plane lattice constant, $\partial E/\partial a$, be zero; the bulk force constants produce a compressive stress which would favor a smaller value of the in-plane lattice constant.

Figure 4. Density of states at $\bar{M}$, weighted by the vibrational amplitude in the surface region, obtained from: (a) the Green's function calculation of Sameth and Mele, and (b) the slab calculation described in the text.

We have used a 300-layer bulk-terminated slab to calculate the vibrational

modes at the Be(0001) surface. The density of vibrational states at $\bar{M}$, weighted by the amplitude in the surface region, is shown in Fig 4a for the Green's function calculation of Sameth and Mele, and in Fig. 4b for slab. The surface modes are clearly visible as two intense peaks separated from the bulk band edge, labeled RW and SH. The displacement patterns inferred from the slab eigenvectors are shown in Fig. 5.

Figure 5. Displacement patterns for surface modes at $\bar{M}$.

The calculated RW (43.5 meV) is even under reflection in the mirror plane and is extremely localized: 95% of the vibrational amplitude is associated with top-layer motion normal to the surface. The calculated SH mode (46.3 meV) is odd under reflection in the mirror plane and is also localized in the top layer (85%). It is appealing to assign the intense loss of Fig. 2 (40.0 meV) to the RW and the weaker loss (50.5 meV) to the SH mode. To first order, the discrepancy in the energy between theory and experiment can be explained by assuming weaker interplanar

bonding and stronger in-plane bonding at the surface, in accord with theoretical predictions [6,7]. Within the scope of the present central-force model, agreement with experiment seems to require the adjustment of two parameters in the surface. An increase in the surface compressive stress, or in the force constant connecting second-nearest neighbors will increase the energy of the SH mode. Additional adjustments must be proposed in order to soften the RW. The dispersion of modes along $\bar{\Gamma}$ to $\bar{M}$ and $\bar{\Gamma}$ to $\bar{K}$ is fairly well reproduced by invoking changes in two of the force constants in the surface layer: a 40% *decrease* in the 1st-nearest neighbor force constant (interplanar) and a 40% *increase* in the 2nd-nearest neighbor force constant (in plane) [12]. Considering the importance of electronic screening at simple metal surfaces, which is completely absent in the central-force model, adjustment of several surface force constants may not give much insight into the underlying physics. Furthermore, in order to make the proposed mode assignment it is necessary to exclude the possibility that the weak loss is due to some other feature in the surface density of states.

The eigenvectors obtained from the slab calculation can also be used to identify the nature of the observed features within the projected bulk bands. For instance, the peak at about 56 meV in Fig 4b is due to a density of sagittal-plane bulk modes, all of which have a small surface amplitude. There are no other features in the range 50 to 65 meV. There is a feature at 51 meV in the *total* slab density of states which represents a clustering of modes that track the projected bulk-band edge from $\bar{\Gamma}$ to $\bar{M}$. This density is comprised entirely of bulk SH modes which have virtually no amplitude in the surface region, and therefore no sharp feature at 52 meV is produced in the *surface* density of states at $\bar{M}$.

Our interpretation of the experimental data is that the weak feature at 50.5 eV in Fig. 2 is the SH *surface* mode, which the bulk-terminated calculations predict to be split-off below the projected bulk-band edge. We attribute the increased width of this feature, compared to that of the intense loss at 39.5 meV, to interaction with the underlying density of bulk SH modes. The assignment of this loss to the SH surface mode is supported by the fact that this mode is not observed when the sagittal plane is carefully aligned so as to coincide with a mirror plane. For such a scattering geometry the displacement pattern for the SH mode is odd under reflection in sagittal plane and excitation is forbidden by symmetry.

In the present EELS investigation of Be(0001) two surface vibrational modes are observed at the $\bar{M}$ -point in the surface Brillouin zone. The energy of the lower mode, the Rayleigh wave, is *lower* than that calculated for a bulk-terminated Be(0001) surface. The upper mode, interpreted as a surface shear vibration, is observed at an energy which is *higher* than that predicted from calculations. Assignment of the modes is made based on the observed symmetry and on an analysis of the eigenvectors and surface density of states calculated using two models: a central force slab model, and a semi-infinite Green's function calculation. The energies of the observed losses are consistent with a "stiffening" of the inplane surface force constant accompanied by a softening of the interplanar surface force constants, in accord with theoretical predictions, however, within the present slab model, agreement with experiment requires the adjustment of two surface force constants. Such ad hoc adjustments may not be unique and are certainly model dependent.

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