

The Unusual Properties of Beryllium Surfaces

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ABSTRACT

Be is a "marginal metal." The stable phase, hcp-Be, has a low Fermi-level density of states and very anisotropic structural and elastic properties, similar to a semiconductor's. At the Be(0001) surface, surface states drastically increase the Fermi-level density of states. The different nature of bonding in bulk-Be and at the Be(0001) surface explains the large outward relaxation. The presence of surface states causes large surface core-level shifts by inducing a higher electrostatic potential in the surface layers and by improving the screening at the surface. Our experimental and theoretical investigations of atomic vibrations at the Be(0001) surface demonstrate clearly that Be screening of atomic motion by the surface states makes the surface phonon dispersion fundamentally different from that of the bulk. Properties of Be(0001) are so different from those of the bulk that the surface can be considered a new "phase" of beryllium with unique electronic and structural characteristics. For comparison we also study Be(11 $\bar{2}$ 0), a very open surface without important surface states. Be(11 $\bar{2}$ 0) is the only clean *s-p* metal surface known to reconstruct (1 \times 3 missing row reconstruction).

I. INTRODUCTION

Beryllium represents an important test of our understanding of bonding in metals.¹ It has no *d* or *f* band near or below the Fermi energy. So it is a "simple" metal. However, Be is not a typical simple metal. For example, the Be-Be bond strength has an unusual dependence on the local atomic geometry. The Be dimer is weakly bound (0.10 eV), with a bond length 11 % longer than the nearest neighbor distance in the

bulk.² In contrast, bulk Be is strongly bound with a cohesive energy of 3.5 eV/atom. The electronic configuration of atomic Be is $1s^2 2s^2$. Bonding in the bulk is achieved via hybridization of atomic s - and p -states. States derived from atomic p -levels experience a dramatic energy-lowering in the bulk environment because overlap with the s -like cores of neighboring atoms (no p cores) is highly favorable. This leads to the small lattice constant and large cohesive energy that characterizes bulk Be. Theoretical studies of Be in reduced dimensionality suggest that the energy gain associated with s - p hybridization is determined by coordination and geometry. An isolated close-packed Be monolayer is relatively strongly bound, with a cohesive energy of 2.94 eV/atom.³ The Be bilayer is characterized by weak inter-planar bonding and strong in-plane bonding, much like a layered crystal.⁴ In addition the equilibrium structure of the Be bilayer has a smaller in-plane spacing than the Be(0001) surface and the inter-planar spacing is expanded.

Despite the fact that Be is s - p bonded, with no occupied d -bands, the band structure is decidedly not that of a free-electron metal. Be is nearly a semiconductor.⁵ In its most common phase (i. e. hcp-Be), Be has a wide band gap in nearly all of the Brillouin zone (BZ).⁶ This leads to a quasi gap in the density of states (see Fig.3) corresponding to the strongly covalent character of the bulk Be-Be bond.⁷

The electronic structure of the Be(0001) surface is dominated by surface states. This is unusual for metal surfaces, whereas it is common for semiconductor surfaces. The reason is that surface states necessarily lie in bulk band gaps. By definition semiconductors have absolute band gaps while metals do not. Be, however, is an exceptional metal with a gap in most of the BZ. Figure 1 shows the band structure of a 13-layer Be(0001) slab. Small dots indicate bulk states, thick dots indicate surface states. The surface states extend over most of the surface Brillouin zone (SBZ) and they cut through the Fermi surface. The intersection of the bulk bands and surface bands with the Fermi energy in the SBZ can be seen in Fig. 2.

The surface electronic structure of Be(0001) has previously been discussed in detail.⁸⁻¹⁰ To give an idea of the accuracy achieved in calculating the surface band structure we compare the energy of the surface state at Γ between the experiments of Bartynski et al.⁸, a LDA calculation by Feibelman¹⁰ and our result. Bartynski and Feibelman find this state in very good agreement at 2.78 eV below the Fermi energy, we get a value of 2.70 eV in reasonable agreement.

The layer-resolved local density of valence states in an 11-layer Be(0001) slab is illustrated in Fig. 3. The shaded region represents the contribution from surface states. The surface states account for about 80% of the density of states at the Fermi energy in the top layer.⁹ The integral of the surface band contribution remains substantial in the second layer and is non-negligible even in the third. A comparison with the density of states in the bulk shows that the Be(0001) surface is much more free-electron-like than bulk Be ($r_s = 1.8$).

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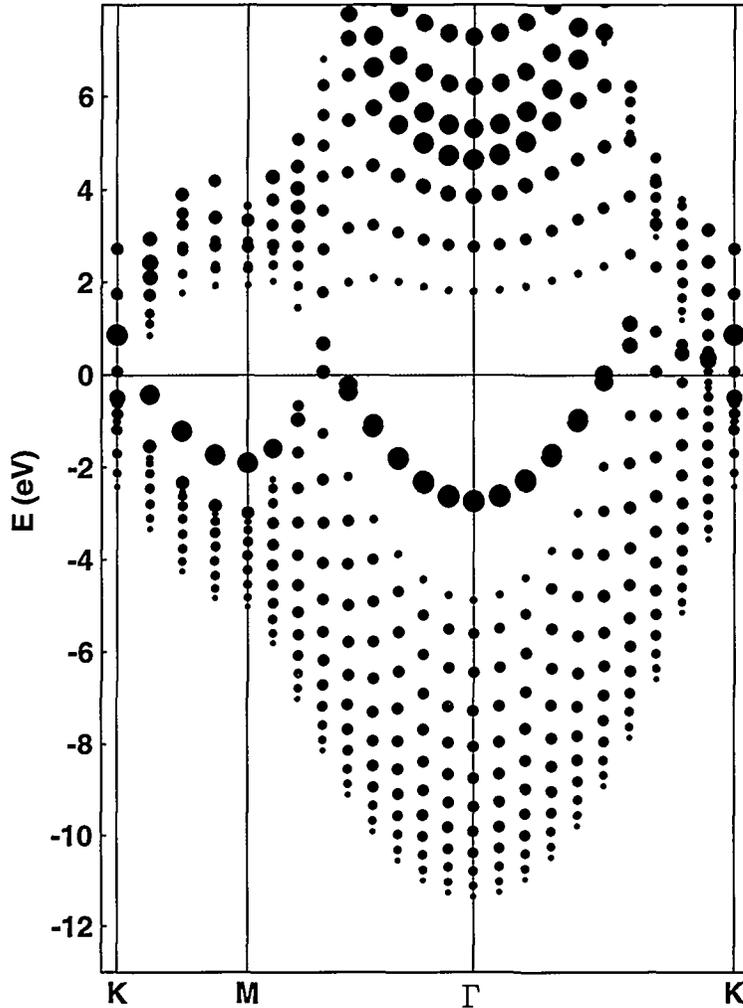


FIG. 1. Calculated band structure of a 13-layer Be(0001) slab. The diameter of each dot describes the surface character of the represented electronic state. The diameter is proportional to the photo yield one would expect coming from that state in a photoemission experiment if exponential attenuation within the slab is assumed. The Fermi energy is at 0 eV.

A. Outline

We review in this paper several of the special properties of the clean Be(0001) surface. Be(0001) has unusually large surface core-level shifts.^{11,12} This is mainly a consequence of surface state induced shifts of the potential in the surface region, but also due to better screening at the surface.¹³ Low energy electron diffraction (LEED) measurements and electronic structure calculations agree that the clean Be(0001) surface relaxes outward significantly.^{10,14,15} The surface phonons of Be(0001) are quite different from the bulk phonons. Both the expansion and the change in phonon

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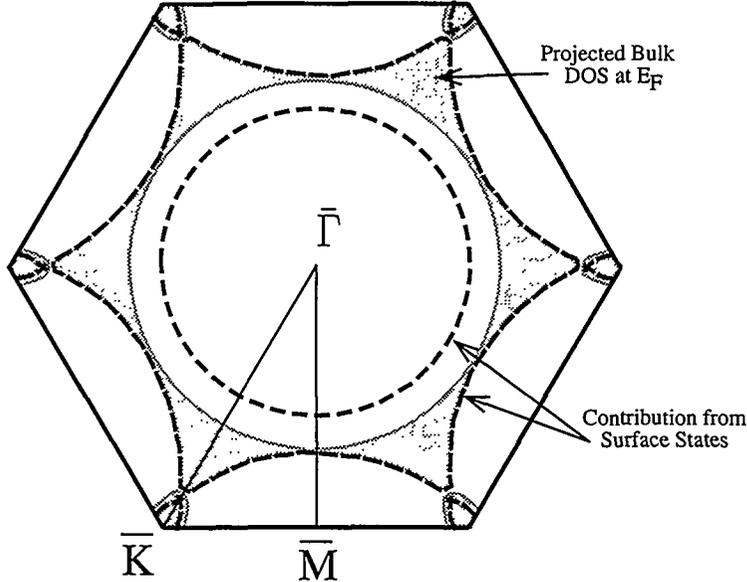


FIG. 2. A picture of SBZ of Be(0001) showing where the bulk and surface bands intersect the Fermi energy as measured by Bartynski et al. by photoemission.⁸

character can be rationalized by assuming that the bonding in the surface is less covalent and more metallic. The phonon dispersion implies that the screening in the surface is more isotropic.

As another example of unusual properties of the Be surfaces we discuss the Be(11 $\bar{2}$ 0) surface. Hannon, Plummer, Wentzcovitch, and Lam (HPWL)¹⁶ have discovered that Be(11 $\bar{2}$ 0) reconstructs, the first clean *s-p*-metal surface to do so. HPWL propose a missing row model for the reconstruction. They have not been able, however, to support this model in a first principles calculation. We will show that better converged calculations lead to better agreement with experiment. We confirm that the missing row structure is the most likely reconstruction by comparison to recent SCLS experiments.¹⁷

II. ELECTRONIC STRUCTURE CALCULATIONS

This study is based on density functional theory (DFT) using the local density approximation (LDA) for exchange and correlation.¹⁸ The electron wavefunctions are expanded in plane waves with an energetic cutoff of 20 Ry. The Be atoms are described by soft separable pseudopotentials.^{19–21}

Generally we use an orthorhombic supercell in our calculations. We use special *k*-points²² and the Fermi surface smoothing technique of Methfessel and Paxton (width of 0.2 eV) to do the Brillouin zone integration.²³ For Be(0001) our *k*-point mesh is equivalent to 72 *k*-points in the irreducible 1/4 of the SBZ of a cell that contains two

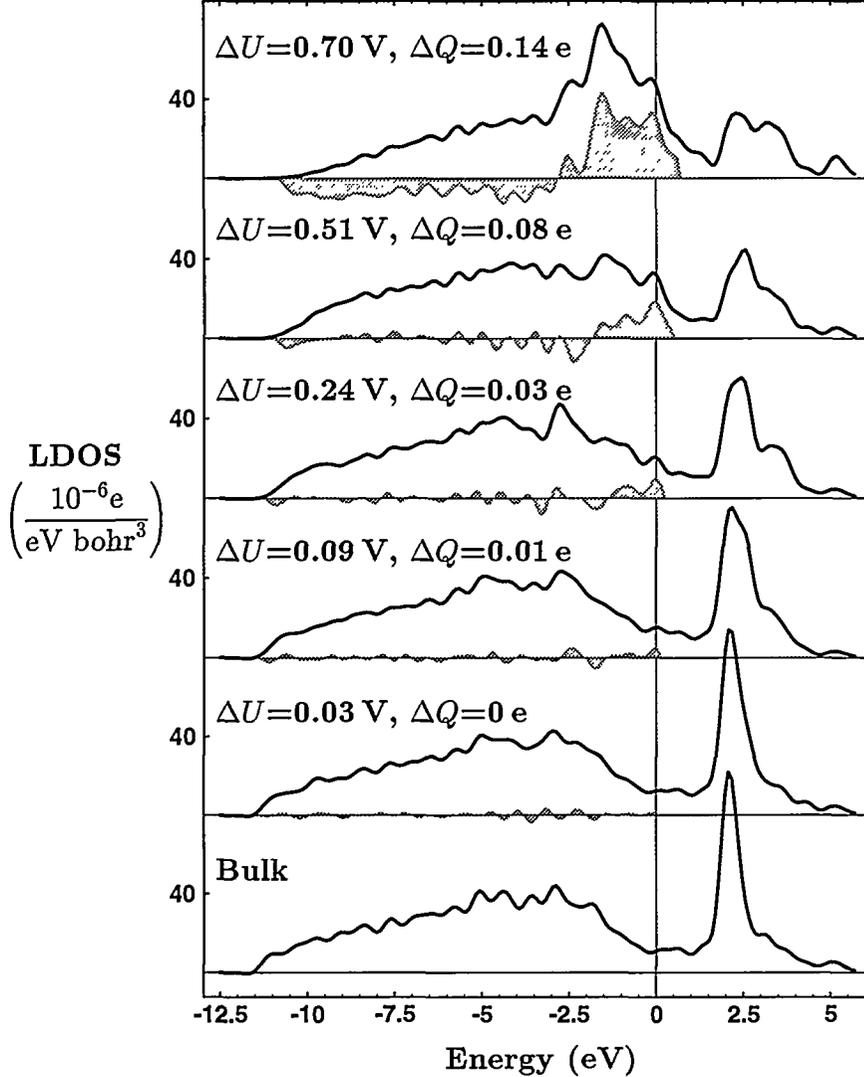


FIG. 3. Layer resolved local density of valence states (LDOS) of a relaxed 11-layer Be(0001) slab. The interfaces between layers are chosen so that the layers contain two electrons per atom. The top panel is for the first layer, the second for the second layer, and so on until the 6th layer which is representative of a bulk layer. The shaded areas represent the change of the LDOS in a surface layer relative to a bulk layer, which is mainly given by the surface states (For the outer layer the band narrowing, because of the reduced coordination, is also important). The shaded area is defined as the difference between the shifted bulk density of occupied states and the LDOS of the surface layer. The magnitude of the shift ΔU is the shift of the effective potential in each layer. For each layer the integral of the shaded area ΔQ gives the number of additional electrons this layer would have per atom if the potential was not shifted.

atoms per layer.²⁴ For Be(11 $\bar{2}$ 0) we use 12 to 16 k-points in the irreducible 1/4 of the SBZ of the 1 \times 3 cell.

The Kohn-Sham equations for the electronic wave functions are solved iteratively using steepest descent.^{25–27} For the calculations of the Be(0001) surface we use a repeated slab of 9 to 13 layers thickness, separated by 5 layers of vacuum. For the SCLS's it is important to have at least 11 layers in the slab. The outer three atomic layers on both sides are relaxed using a damped Newtonian dynamics technique.²⁷ The Be(11 $\bar{2}$ 0) slabs are 11 to 15 layers thick, separated by 5 vacuum layers. In this case 4 to 6 layers on each side are allowed to relax. The two surfaces of the slabs are equivalent by symmetry; we force mirror symmetry relative to the center plane of the slab.

This procedure gives values of lattice constants a and c and Poisson ratio ν_P of $a = 4.23$ bohr, $c/a = 1.573$ and $\nu_P = 0.025$, which are reasonable compared to the experimental values of $a = 4.32$ bohr, $c/a = 1.567$ and $\nu_P = 0.02 - 0.05$.^{6,28,29} Note that the c/a ratio is about 4 % smaller than the ideal c/a ratio corresponding to close packing of spheres. Also note the extremely small Poisson ratio.

III. SURFACE CORE LEVEL SHIFTS ON BE(0001)

Like many of the properties of Be, the core-level spectra, as revealed by a X-ray photoemission spectroscopy (XPS) experiment by Johansson et al.,^{11,17,30} are unusual. Unlike Al(111), a close-packed simple metal surface whose core level shift is zero within experimental error,³¹ there are three surface core level features at Be(0001) whose energies are shifted higher relative to the bulk peak by 0.83 eV, 0.57 eV, and 0.27 eV.¹¹ Another appropriate comparison is the Mg(0001) surface where the surface core level shift is less than 0.1 eV.³² These surprisingly large SCLS's for Be(0001) have been investigated theoretically, with results in qualitative agreement with the XPS results.^{12,13,33} Our calculations give four surface core level shifts of 0.94 eV, 0.67 eV, 0.29 eV, and 0.09 eV in nearly quantitative agreement with the experiment.³⁴

A. Initial state effects

We interpret the large core level shifts of Be(0001) in terms of the large electron population at the surface that resides in surface states.¹³ The basic idea is similar to the usual explanation for the SCLS trend in the transition metal series. There one argues³⁵ that because a surface atom has fewer neighbors than a bulk atom, the LDOS in the surface is narrower. Since the Fermi level is the same in all layers, and since strong electrostatic forces impose layerwise charge neutrality, the surface layer LDOS must shift. If the Fermi energy lies higher than mid-band for example, the narrower LDOS must shift to lower binding energy so that it will not be overpopulated. The

	1.layer	2.layer	3.layer	4.layer
experimental	0.83	0.57	0.27	
electrostatic	0.66	0.50	0.23	0.09
exchange-correlation	0.04	0.01	0.00	0.00
screening	0.24	0.16	0.06	0.00
full SCLS	0.94	0.67	0.29	0.09

TABLE I. Experimental and theoretical core level shifts of Be(0001). The experimental results are from Ref. 11. The theoretical results are for the 11-layer slab of Fig. 3. The initial state shift (electrostatic and exchange-correlation) is calculated directly, the full SCLS is determined from a Boron impurity calculation, and the final state or screening shift is just the difference between those two. All shifts are in eV.

electrostatic fields that shift the surface layer LDOS's, and thus enforce local charge neutrality, are also sensed by the core electrons. This accounts for the "initial state" contribution to the SCLS in the transition metals. The band narrowing model is however incapable of explaining SCLS's in the second and deeper layers. Their atoms are fully coordinated and, therefore, there is practically no band narrowing. Thus a different, if related, explanation of the Be(0001) core-level spectrum is necessary.

If one examines the layerwise resolved local density of states of Be(0001), one sees especially at and below the Fermi level that it is much higher in the outer two crystal layers than in the interior (see Fig. 3). This supplemented LDOS in the surface layers has two effects. If the surface LDOS were not shifted to lower binding energy by some additional field at the surface, then charge neutrality would be violated at the surface. We calculate this potential shift ΔU for each layer as the expectation value of the effective potential for core-electrons of atoms of that layer. Table I shows that the largest part (0.66 eV of a total shift of 0.70 eV) of this potential shift is electrostatic and the rest due to exchange and correlation (XC) effects. The sign of the XC-shift tells us that the valence charge density in the core region is slightly reduced at the surface, which means that the valence charge density is more extended at the surface than in the bulk. This can also be seen in charge density plots of the surface region as compared with the bulk.^{10,14}

Given the potential shift ΔU , one can calculate approximately the excess integrated density of states ΔQ in a surface layer if the shift were not there. This is done by subtracting the shifted bulk LDOS from the surface LDOS and integrating the result, the shaded area in Fig. 3, up to the Fermi energy plus the shift. The first layer for example would contain 0.14 excess electrons per atom if the potential were not shifted in the surface layer.

B. Final state effects

The upward shift of the potential at the surface, i. e. the initial state effect can qualitatively explain the observed upward SCLS's of the non-*d*-band metal Be. Final state, or screening effects in the surface layer of a metal are not expected to be very different from the bulk. Electronic screening affects the SCLS by reducing the energy of the core hole. Screening is mostly performed by electrons which are close to the Fermi energy because they require the smallest energy to polarize toward the core-ionized Beryllium atom. The larger LDOS at the Fermi energy in the outer layers therefore enhances the screening in those layers.

The final state or screening contribution to the SCLS is determined as the difference between the calculated full SCLS and the initial state contribution alone. The full SCLS can be calculated from first principles within the “equivalent core” or “Z+1” approximation.³⁶ In this approximation, the core-ionized Be atom is represented as a substitutional B-impurity. In our slab calculations, we get the full SCLS by comparing the energy of a B-impurity in the center layer and in a surface layer of the Be(0001) slab.³⁷ In these calculations, the atomic geometry is not allowed to relax around the B impurities, in order to match the experimental situation in which the electron emission occurs. In experiment the atomic relaxation usually does not happen during the short time the core hole exists. For the top layer the full SCLS is 0.94 eV. Thus the final state shift due to screening is 0.24 eV toward a smaller ionization potential of the core states at the surface.

IV. SURFACE STRUCTURE

A. Expansion of the Be(0001) surface

Be(0001) shows a large outward relaxation. This was first established in a LEED analysis by Davis et al.¹⁵ (see Table II) where an expansion Δd_{12} of the first inter-layer spacing of 5.8 % was found (1 Subsequently outward relaxation was also found in calculations using the LDA by Feibelman¹⁰ ($\Delta d_{12} = 3.9\%$) and the generalized gradient approximation (GGA) by Holzwarth and Zeng¹⁴ ($\Delta d_{12} = 2.5\%$). Our calculations find a top layer expansion of Be(0001) of 2.7 %.

The quantitative agreement of the different results is not as good as usual for modern LEED analysis and electronic structure calculations. The difference between LEED and LDA could be due to a neglect of temperature effects in the calculations. While bulk phonon measurements indicate that anharmonicity is not a large effect in the bulk³⁸, it is conceivable that anharmonicity might be significantly enhanced at the surface, so that at room temperature, where the LEED data were taken in Ref. 15, the surface additionally expands. In order to explore this possibility, the LEED measurements have recently been repeated at 90° K by Pohl et al.³⁹ Apart from a

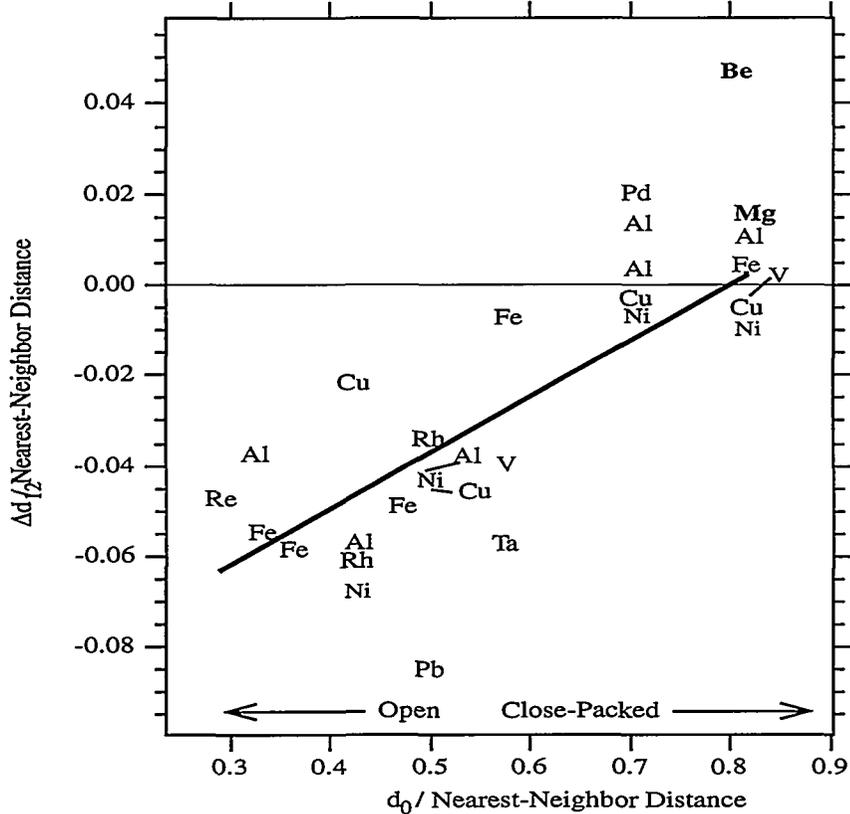


FIG. 4. Comparison of the top layer relaxation Δd_{12} relative to the bulk nearest neighbor distance and the openness of the surface, which is measured by the ideal layer separation divided by the bulk nearest neighbor distance. The figure is after Davis et al.¹⁵

smaller Debye-Waller factor, the data from low- and room-temperature experiments are in quantitative agreement, indicating that the discrepancy between theory and experiment is not due to temperature effects. Nor is it caused by a failure of LDA, as the comparison to the GGA results shows.

The larger value for the expansion in the LAPW calculation as compared to the two other calculations is due to an insufficient k-space sampling used before.¹⁰ The surface relaxation of Be(0001) is, like the SCLS of Be(0001), very sensitive to k-space sampling. We assume that the sensitivity is caused by the large contribution to the Fermi LDOS by surface states concentrated around the \bar{K} point of the Brillouin zone (see Fig. 1). An additional factor that makes the relaxation very sensitive is that the energy gain by relaxation, 6 meV/atom or equivalent 1.4 meV/Å², is rather small.

Though we do not get fully quantitative agreement between experiment and theory, there is no doubt that the Be(0001) surface exhibits a large outward relaxation of the outer layer. In addition the calculations tell that the interlayer spacing falls off only slowly towards the bulk value. We interpret this fact as a consequence of the

relaxation	Δd_{12} (%)	Δd_{23} (%)	Δd_{34} (%)
LEED ¹⁵	5.9	-.2	0.2
this work	2.7	1.2	0.6
LAPW (LDA) ¹⁰	3.9	2.2	
PWPP (GGA) ¹⁴	2.5		

TABLE II. Relaxation of outer layers of Be(0001) according to LEED analysis by Davis et al. and to electronic structure calculations. The linear augmented plane wave (LAPW) calculations of Feibelman and the plane wave pseudopotential (PWPP) calculations within the GGA by Holzwarth and Zeng used nine-layer slabs, our results are averages for slabs with eleven and thirteen layers.

mechanism that drives the surface expansion.

The large outward relaxation is unusual, considering that close-packed fcc(111) surfaces exhibit only small surface relaxations, the largest expansion being the 0.9–1.7% increase at the Al(111) surface.⁴⁰ This can be seen in Fig. 4 where we display what has been called the universal curve.¹⁵ Fig. 4 shows the measured relative change of the top layer spacing as a function of the openness of the surface. The only hcp(0001) surface which clearly expands is Mg(0001). The outer layer expansion is 1.9% according to LEED⁴¹ and 1.5% according to LDA calculations.⁴² We now wish to give an explanation for the expansion in the special case of Be(0001).

The outward relaxation is caused by the different nature of bonding in bulk Be and at the surface. Bonding in bulk hcp-Be is anisotropic. The bond length in the basal plane (i.e., the x - y plane) is about 3% larger than in the perpendicular direction. Therefore the c/a ratio is about 4% smaller than ideal. Related to that, the elastic properties are also very anisotropic,²⁹ as is clearly shown by the extremely small Poisson ratio ($\nu_P \leq 0.05$) and the character of the phonon dispersion which we discuss below.

The situation at the Be(0001) surface is very different from the bulk. The Fermi density of states is very close to the free-electron value in the surface layer and is still higher than in the bulk for the second and third layer (see Fig. 3). The bonding character at the surface, therefore, is much more metallic than in the bulk. This leads to the better screening at the surface and the more extended charge density which we discussed already for the SCLS's. The more metallic character of the Be(0001) surface also favors more isotropic bonding, which means that the c/a -ratio should be closer to the ideal c/a -ratio. Since a is fixed this means that the inter-layer spacing expands. Since the Fermi density of states is also enhanced in the second and third layer even the second and third inter-layer spacing expand.

The surface expansion is accompanied by a weakening of the inter-planar bonds. We find that the force constant for vertical displacement of the top layer on Be(0001) relative to the second layer is by 20% smaller than for the displacement of the third

layer relative to the fourth.

In order to compensate for the longer and weaker inter-plane bonds the intra-plane bonds want to contract.⁴³ This would also reduce the local c/a -ratio. Shorter intra-plane bonds are, however, not an option because the bond length is fixed by the bulk lattice constant without surface reconstruction. Thus the surface is under a rather large tensile stress of about $0.2\text{eV}/\text{\AA}^2$ according to our calculations. This value for the stress is more than twice that of Al(111) and even larger than that of Au(111), a surface which is known to have a reconstruction driven by the surface stress.⁴⁴ Be(0001) is stable against such a reconstruction because of the 6.5 times larger shear modulus as compared to Au. A strong resistance against shear counteracts a compressive reconstruction.⁴⁴ It has to be expected however that the dispersion of the surface phonon modes will be influenced by the tensile stress,^{44,45} the screening of the surface states and the interplanar expansion.

The mechanism driving the expansion of Be(0001) is special for the marginal metal Be. The expansion of Al(111) and Mg(0001) must have a different driving force. Both, Al and Mg, are good metals in the bulk, with a high Fermi density of states and rather isotropic bonds. Surface states are much less important on Al(111) and Mg(0001).^{9,46}

B. Missing row reconstruction of the Be(11 $\bar{2}$ 0) surface

The open Be(11 $\bar{2}$ 0) surface presents a sharp contrast to the close packed Be(0001) surface. On Be(11 $\bar{2}$ 0) there are no important surface states.^{47,48} Furthermore, there is a (1 \times 3) reconstruction at all temperatures investigated by HPWL¹⁶ (100° K to 750° K). This is interesting in that Be(11 $\bar{2}$ 0) is the “only” clean simple-metal surface known to reconstruct.⁴⁹

A simple kinematic analysis based on the work by Henzler,⁵⁰ indicates that the surface consists of an ordered array of single-step height, up- and down-terraces of uniform width.¹⁶ A recent dynamical I - V analysis has confirmed these results.³⁹ The structure that leads to the best agreement between the measured and the calculated I - V curves corresponds to the removal of every third row of atoms along the [0001] direction (see Fig. 5).

Missing-row (MR) reconstructions have been observed at the fcc(110) surfaces of noble- and transition-metals. First principles calculations for the Au and Ag(110) surfaces indicate that the stability of the MR is related to the properties of the occupied d -band, specifically to the reduced energy gain by d - d hybridization at the surface.⁵¹ However, Be possesses *no occupied d -bands* so the mechanism of reconstruction must be different.

There are two previous calculations of the Be(11 $\bar{2}$ 0) surface, one using the embedded atom method (EAM), by Chen,⁵² and one within LDA by HPWL¹⁶ (see Table III). In both calculations the bulk terminated (BT) surface has the lowest en-

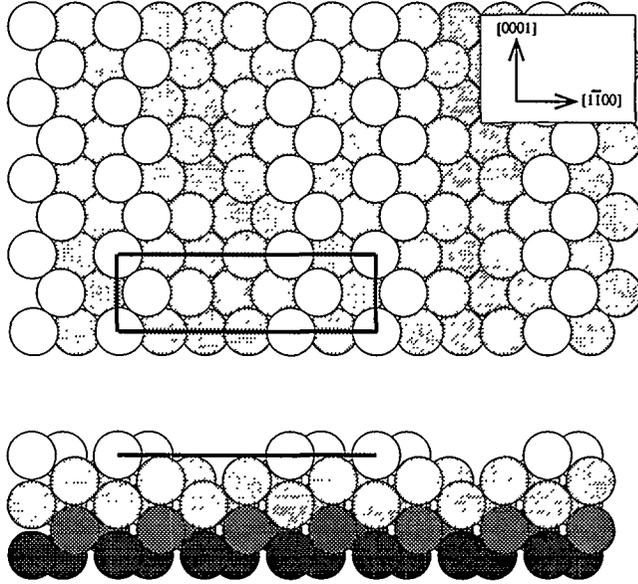


FIG. 5. Top and side view of a missing-row (MR) reconstructed hcp($11\bar{2}0$) surface. The 1×3 surface cell is indicated.

	unrelaxed				relaxed			
	BT	MR	AR	MF	BT	MR	AR	MF
Chen (EAM) ⁵²	112	118		127	110	116		125
HPWL (LDA) ¹⁶	152	164		156				
Present work (LDA)	153	156	157		148	149	149	154
Au(110) (LDA) ⁵¹	89	87			86	82		

TABLE III. Calculated surface energies (in $\text{meV}/\text{\AA}^2$) for models of Be($11\bar{2}0$) and, for comparison, of Au(110). BT is an abbreviation for bulk-terminated, MR for missing-row, AR for added-row, and the MF structure consists of ($10\bar{1}0$)-microfacets. All reconstructions have 1×3 symmetry and leave the zig-zag chain of surface atoms intact. Compare to the surface energy of relaxed Be(0001) of $129 \text{ meV}/\text{\AA}^2$ in our calculations.

ergy. The energy difference between the BT and the other models is quite large, as a comparison to the Au(110) results shows (Au(110) exhibits a MR reconstruction). Obviously the calculations give wrong answers. EAM calculations are not supposed to be really quantitative, but the LDA first principles calculations should get the energy differences right. It was argued by HPWL¹⁶ that if the surface was relaxed, the reconstructed surfaces could be favorable.

We do the relaxed calculation, increasing the slab thickness and the basis set relative to HPWL¹⁶. Six different 1×3 reconstructions of the removed atom type are considered. In agreement with experiment we find that the zig-zag chains are quite stable. All 1×3 models, where one of the chains is broken by removing a surface atom,

surface shift	#1	#2	#3	#4	#5
XPS ¹⁷	0.41				
BT	-0.37	0.375	-0.01		
MR	-0.12	0.48	0.04		
AR	0.07	-0.40	-0.23	0.42	-0.05

TABLE IV. Measured and calculated SCLS's of reconstructed and unreconstructed Be(11 $\bar{2}$ 0) in eV.

have surface energies of at least 183 meV/Å². Among those structures with the chains intact three structures have practically the same surface energy (148 meV/Å² for the BT surface, 149 meV/Å² for the MR and AR reconstructions; see Table III). The MF surface is about 5 meV/Å² higher in energy. In order to find out if the reconstructions are driven by the atomic relaxation we calculated also the energy for the unrelaxed case. We find that the relaxation energy is smaller for the BT surface as compared to the MR and AR surfaces (5 meV/Å² for BT and 7–8 meV/Å² for MR and AR).

Recently Johansson et al.¹⁷ measured the SCLS's for the Be(11 $\bar{2}$ 0)-(1×3) surface. For comparison with their results we compute the initial state contributions to the SCLS's of the Be(11 $\bar{2}$ 0)-(1×3) models investigated (see Table IV). Johansson et al. find a single, rather broad surface feature at 0.41 eV, i. e. at reduced core state binding energy. If we assume that the final state effects are not bigger than for Be(0001), which is reasonable because of the absence of surface states on Be(11 $\bar{2}$ 0), we conclude that only the MR model is consistent with experiment. Both, the BT and the AR model have SCLS's for some atoms at about -0.40 eV which would be clearly detectable in experiment. The -0.12 eV feature of the MR structure quite likely is hidden in the broad peaks of the experiment. It is worth noting that for the MR model only “second” layer atoms show a large SCLS. We will discuss this observation and the origin of the SCLS's of Be(11 $\bar{2}$ 0) elsewhere.⁴⁸

Having identified the MR reconstruction as the most likely candidate for the surface reconstruction we are left with the question of why it is energetically not really favored in our calculations? We first note that there should not be a big difference in energy between the MR and, say, the BT or AR structures. HPWL find by analyzing their LEED data that the 3×1-Be(11 $\bar{2}$ 0) surface is much less well ordered in the direction perpendicular to the chains than parallel to the chains.¹⁶ So we need only a small energy contribution not considered in our calculations yet which should favor the MR structure. One candidate is the GGA which is known to favor systems with a larger surface area like the MR as compared to the BT surface. Perhaps also the lattice vibrations, at zero and finite temperature, can account for energy differences of the order needed to make the MR phase the stable one. We have to admit, however, that we do not know the energetical reason for the reconstruction yet.

V. BULK VERSUS SURFACE PHONONS

The special bonding character at the Be(0001) surface, which is dominated by the high density of surface states, leads to an outward expansion of the surface layer and to the tensile surface stress. More can be learned about the bonding at the surface from an investigation of the dynamical properties of the surface: from surface phonon dispersion. When an atom is displaced from equilibrium, the local rearrangement of the valence charge leads to a restoring force directed against the displacement. In the simplest conceptual picture, the interatomic potential is a sum of pair-wise central interactions. Central-force (CF) models have been widely used in calculating the bulk and surface phonon dispersion of metallic systems. However, for systems where the charge density is inhomogeneous, for example semiconductors, CF models are not as successful. For these systems, the inhomogeneous valence electronic density acts as a third body which gives rise to indirect ion-ion interactions. These interactions often take the form of phenomenological three-body potentials, for example "angle-bending" forces or interaction with "bond charges". For metallic systems, indirect ion-ion interactions can be conveniently addressed within the framework of electronic screening. When an atom is displaced, the valence charge density screens the perturbing electric field. The induced field, in turn, acts upon the ion cores.

Non-central forces can be expected to be important for metallic systems which exhibit anisotropic screening. As Eguiluz et al. have pointed out,⁵³ non-central forces are expected to be enhanced at metal surfaces because the abrupt termination of the charge density at the surface is inherently anisotropic. Enhanced non-central forces have been invoked in order to explain the dispersion of phonons at Ni surfaces.⁵⁴

Be is unlike nearly all metallic systems in that non-central forces are important for even a qualitative description of lattice dynamics in the bulk. Roy et al.⁵⁵ have shown that CF models are incapable of producing the correct ordering of bulk phonon modes. If the bulk phonon dispersion is calculated assuming pair-wise, non-central interactions, one finds that the largest non-central forces are associated with neighboring atoms within the (0001) planes. The dominant non-central interaction can be visualized by considering the displacement of an atom (A) parallel to the bond linking A to an in-plane neighboring atom, B. One can easily see from symmetry considerations, that in a CF model, the resultant force on atom B is directed along the bond. However, in bulk Be, the force on atom B possesses components both parallel and perpendicular to the bond. The perpendicular component of the force arises because the in-plane electron density is anisotropic: when atom A is moved towards atom B, atom B prefers to move so as to avoid the tetrahedral hole. The non-central nature of this interaction is most-likely related to the anisotropic charge density within the Be(0001) planes: charge builds up in the tetrahedral holes.^{6,14}

We have measured the dispersion of phonons at the Be(0001) surface in order to understand the influence of the large density of surface states on dynamics of surface

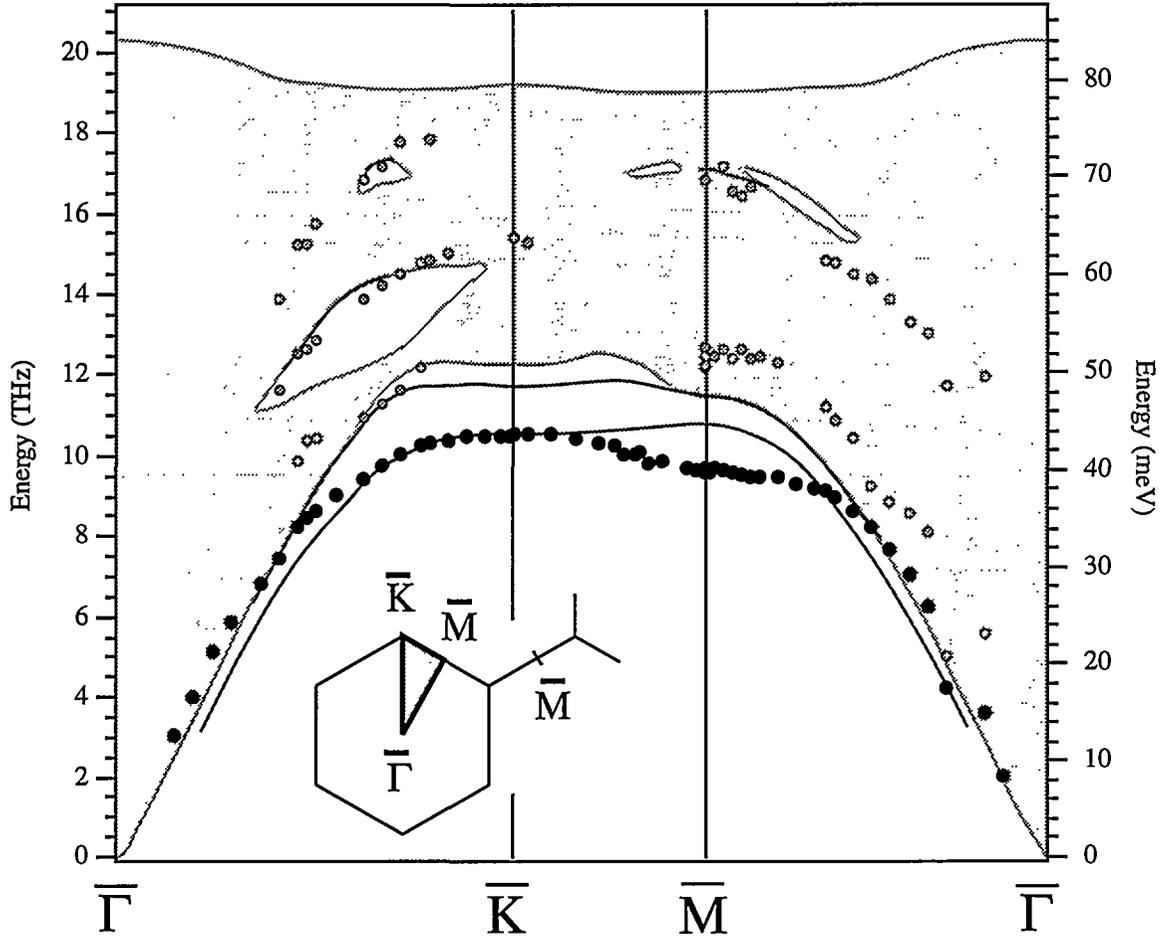


FIG. 6. Experimental surface phonon dispersion (circles; filled circles indicate Rayleigh wave) superimposed on the dispersion of modes of a 100-layer bulk terminated Be(0001) slab determined using the non-central force model.

atoms. The density of states at the Fermi energy, at the surface, is five times larger than that of bulk Be (see Fig. 3). Consequently, the non-central forces arising from electronic screening differ significantly at the surface, because the charge density of the surface (0001) planes is more isotropic than that of bulk Be. The Be(0001) surface is a high-density free-electron metal, whereas bulk Be is nearly semiconducting. The result is that the dynamics of surface atoms resembles that of bulk Mg more than that of bulk Be.⁵⁶

The measured vibrational modes of the Be(0001) surface are shown in Fig. 6 (filled circles), superimposed on those calculated for a 100-layer, bulk-terminated Be(0001) slab. The model potential consists of pair-wise, non-central interactions out to the seventh-nearest neighbor shell. The parameters of the model were determined from a fit to the measured bulk phonon dispersion.³⁸ The shaded area corresponds to the projection of bulk phonon bands onto the (0001) surface, and the solid lines are the

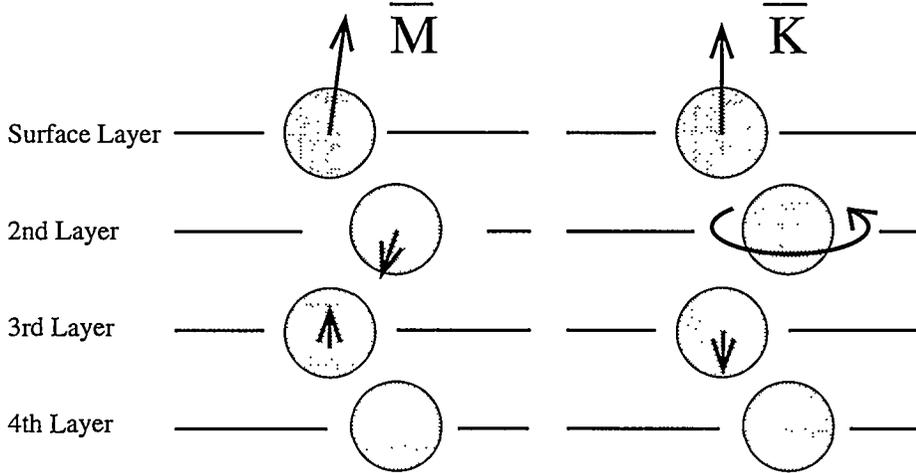


FIG. 7. Displacement pattern of the Rayleigh wave at the \bar{M} and \bar{K} point of the surface Brillouin zone of Be(0001) according to the model potential calculation described in the text.

calculated surface modes.

Our analysis is focused on the dispersion of the lowest-energy surface mode, split-off below the bulk-band edge. This mode is the Rayleigh wave (RW), and can be calculated in the long-wavelength limit using continuum elasticity theory. As the wavelength of the RW is reduced, the displacement pattern becomes more localized at the surface. At the zone boundary (\bar{K} to \bar{M}), the displacements are confined to the top two surface layers, with most of the displacement corresponding to top-layer motion normal to the surface. The displacement pattern associated with the RW at \bar{K} and \bar{M} are shown in Fig.7. The RW at \bar{M} is even under reflection in the mirror plane of the surface, and consequently the motion is confined to the sagittal plane. However, the \bar{K} point is not contained within a mirror plane; the second layer atoms exhibit circular in-plane motion which is reminiscent of the bulk vibrational modes at \bar{K} .

The most significant discrepancy between the bulk-terminated theory and the measured RW dispersion is the sign of the dispersion from \bar{K} to \bar{M} . The experimental dispersion from \bar{K} to \bar{M} is negative, whereas the calculated dispersion is positive. One can conclude immediately that the dynamics of the surface region is quite different from that of "bulk-terminated" Be(0001). We have systematically modified the model parameters in order to understand the physical mechanism for the reversal of the ordering of modes at \bar{K} and \bar{M} . It is common that the bonding at metal surfaces is weaker due to the reduced coordination of surface atoms. Measured surface phonon dispersion is often compatible with a softening of the central interactions at a surface, and our first principles calculations suggest that there is a 20 % softening to the interplanar coupling between (0001) planes at the surface. Nevertheless simple modification of the central parts of the interactions cannot induce a reversal of the sign of

the dispersion from \bar{K} to \bar{M} . Because the displacement patterns of the RW at \bar{K} and \bar{M} are similar, modification of the central forces tends to rigidly shift the dispersion at the zone edge. The most physically-reasonable way to induce a reversal of the ordering of the modes at \bar{K} and \bar{M} is to replace the non-central, in-plane interaction with a purely *central* interaction of similar magnitude. This modification produces an anisotropic response in the surface phonon dispersion: the circular motion of the RW at \bar{K} is sensitive to perpendicular in-plane coupling, whereas the RW at \bar{M} is not. Furthermore, this modification is in accord with our understanding of the Be(0001) surface: the surface is a high-density free-electron metal, more like bulk Mg, whereas bulk Be is nearly semiconducting. The surface states contribute an isotropic density of states which is 5 times larger than that of bulk Be at the Fermi energy.

VI. CONCLUSIONS

Beryllium is indeed a unique material, offering a testing ground for concepts and techniques in surface physics. Bulk hcp-Be is a marginal metal. Its Fermi level density is very low and its elastic properties are like a semiconductor's. The properties of the Be(0001) surface are strongly influenced by the presence of surface states. They are the reason that the non-*d*-metal Be has SCLS's of up to nearly 1 eV in magnitude at the (0001) surface. The additional density of states due to surface states raises the potential at the surface and enhances the screening. Be(0001) has a strong outward relaxation of its outermost atomic layers and at the same time a large surface tensile stress, both due to the change in bonding character.

The Be(11 $\bar{2}$ 0) surface, which is the most open of the low index surfaces, has a 1×3 missing row reconstruction. This is shown by a comparison between theory and experiment. However, the driving force for this reconstruction is still not understood.

A non-central force model has been used to investigate the effects of surface stress and modified bond-strength on the surface vibrational modes. A comparison with measured phonon dispersion curves shows that for the description of the surface the model parameters derived for the bulk give a poor description of the surface. The fact that the intra-plane non-central components have to be reduced to get a good description of the surface phonon dispersion again corresponds to the more metallic character of bonding in Be(0001) as compared to the bulk.

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