Anomalous Interplanar Expansion at the (0001) Surface of Be

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Analysis of low-energy electron diffraction spectra for Be(0001) shows that the interplanar spacing between the first and second planes is expanded by 5.8% or 0.10 Å. The size of this expansion is large compared to that of close-packed fcc (111) surfaces, which show little or no expansion. This large expansion is discussed in terms of the unique bonding of Be. The second and third interplanar spacings show almost no relaxation.

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This paper reports an abnormally large *expansion* of the first interplanar spacing for the Be(0001) surface; i.e., an *expansion* of 5.8%, or 0.10 Å, has been obtained by the analysis of low-energy electron diffraction (LEED) intensity versus kinetic-energy (*I-V*) spectra. This result should be compared to the close-packed fcc (111) surfaces, which show little relaxation, and the *contractions* which have been found for the (0001) faces of other hcp crystals [1]. Before documentation of the results for Be(0001), however, it is instructive to provide a perspective of surface interplanar relaxation.

When a solid is divided to create two surfaces, the atoms in the proximity of the surface are exposed to appreciably different forces from those on bulk atoms. This is an obvious consequence of reduction in symmetry and loss of neighbors. The atomic positions of the ideal, bulk-terminated surface do not necessarily minimize the free energy; as a result, the positions of surface atoms are usually different from that of the ideal surface. In an extreme case the surface reconstructs, forming a two-dimensional array which differs from the bulk structure, but the most common response is interplanar relaxation [2]. The advancement of experimental techniques such as LEED and ion scattering has shown that measurable interplanar relaxation exists for almost all metallic surfaces, with a contraction of the first interplanar spacing being the general rule, accompanied by damped oscillatory relaxation of deeper spacings. For more open crystal faces the contraction is usually larger, and the relaxation extends deeper. But the oscillatory relaxation does not have to be commensurate with the lattice. One example is Al(331) where substantial relaxations of the first four spacings exist [3]: The spacing $d(12)$ between the first and second atomic planes has a relative relaxation $\Delta d(12) = -11.7\%\ d_0$ (contraction), $\Delta d(23) = +4.1\%\ d_0$ (expansion), $\Delta d(34) = +10.3\%\ d_0$, and $\Delta d(45) = -4.8\%\ d_0$, where d_0 is the bulk spacing.

Oscillatory interplanar relaxation is such a general property of metal surfaces, with obvious repercussions on the static and dynamic properties, that it has attracted considerable theoretical interest. Its theoretical complexity is easily illustrated by the contradictory results obtained by Gupta [4] and by Finnis and Heine (FH) [5]. Gupta showed that classical interatomic potentials (Morse, Lennard-Jones, etc.) quite generally yield an expansion of $d(12)$. However, in a key paper FH applied the concept of surface charge smoothing (developed by Smoluchowski [6] to explain work-function variations), which creates an electrostatic force that causes $d(12)$ to contract. But the FH "point-ion model" has proven to be too simple for quantitative predictions, and it overestimates the contraction. Landman, Hill, and Mostoller [7] generalized the model by the inclusion of a more realistic charge profile normal to the surface, which leads to oscillatory interplanar relaxation. Further improvements have incorporated self-consistent one-dimensional [8] and three-dimensional [9] charge profiles, and a phenomenological electronic restoring force [10] to overcome some limitations of the point-ion model. Smith and Banerjea [11] have used an "equivalent-crystal theory" to compute relaxation for several low-index metallic surfaces, and obtained $d(12)$ contractions for all surfaces (2.9% to 10%) with expansions of $d(23)$ and $d(34)$. Calculations [12] of relaxation for several transition and noble fcc metals, based on the embedded-atom method, have yielded $d(12)$ contractions of (2–3)% for (111) surfaces and up to 12% for (110) surfaces.

Self-consistent local-density-approximation calculations (SCLDAC) have been published for a few specific surfaces [Al(110) [13–15], Al(100) [14,16,17], Al(111) [15,18], and W(100) [19]]. Two general conclusions, which differ from the more phenomenological calculations described above, can be drawn from the SCLDAC. First, the SCLDAC yield small $d(12)$ *expansions* for the densest faces. Second, the self-consistent screening makes the oscillatory relaxation incommensurate with the lattice, because the length scale of the electron response is associated with the Fermi wave vector [14]. This behavior is present in the 1970 jellium-based calculation of Lang and Kohn [18], which predicted an expansion of 0.5% in $d(12)$ for Al(111), in reasonable agreement with the 1.7% expansion obtained in a recent LEED analysis [20]. It is also noteworthy that a 1.0% expansion was predicted by self-consistent calculations of Needs [15].

A Be(0001) sample was cut and polished using procedures described previously [21], and then inserted in an ultrahigh-vacuum chamber with a base pressure of 5×10^{-11} Torr. It was cleaned by cycles of 20-min sputtering with 1-keV Ne ions (approximately 15 $\mu A/cm^2$) followed by 30-sec anneals to 450 °C. Adsorption of contaminants was characterized by high-resolution electron-energy-loss spectroscopy. LEED I-V spectra for the (10), (11), and (20) beams were measured using reverse-view optics controlled by a video data-acquisition system [22]. The Be Debye temperature of ~1500 K allowed all data to be collected at room temperature. If the electron gun illuminated only one of the two possible terminations of Be(0001), the observed diffraction pattern should have had threefold symmetry. However, the experimental pattern had sixfold symmetry, which indicated an average over the two possible terminations.

Calculated I-V spectra were obtained from computer codes [20] which were based on the layer Korringa-Kohn-Rostoker formalism and renormalized-forward-scattering perturbation theory. In order to ensure numerical convergence, the calculations used a 12-atomic-layer slab, up to 13 phase shifts, and 85 reciprocal-lattice vectors. The phase shifts were obtained from the Be potential tabulated by Moruzzi, Janak, and Williams [23]. The calculated and experimental spectra were compared by use of the R_2 factor, which is the mean square of the difference between the spectra [24].

Figure 1 illustrates the variation of the total R_2 factor, and that for the individual beams, as a function of $\Delta d(12)/d_0$ ($d_0 = 1.79$ Å). Each of the curves in Fig. 1 shows minima in R_2 for an expansion of close to 6%, and none of the curves indicates another minimum for a contraction in $d(12)$. Figure 1 is a final result of an iterative procedure, where first a minimum in the total R_2 was found as a function of $\Delta d(12)$, then the nonstructural parameters (the complex optical potential and layer Debye temperatures) varied to minimize R_2, followed by a search for improved interplanar spacings. This procedure was repeated until the final minimal $R_2 = 0.0261$ was achieved for

$$\Delta d(12) = (+5.8 \pm 0.4)\%\ d_0,$$

$$\Delta d(23) = (-0.2 \pm 0.5)\%\ d_0,$$

and

$$\Delta d(34) = (+0.2 \pm 0.5)\%\ d_0.$$

The errors were determined from extensive variation of the parameters, both structural and nonstructural. For comparison, the minimal R_2 achieved for Al(111) [20] was 0.0191 and for Cu(100) [25] was 0.0198. Thus, the minimal R_2 here is comparable to those of good LEED

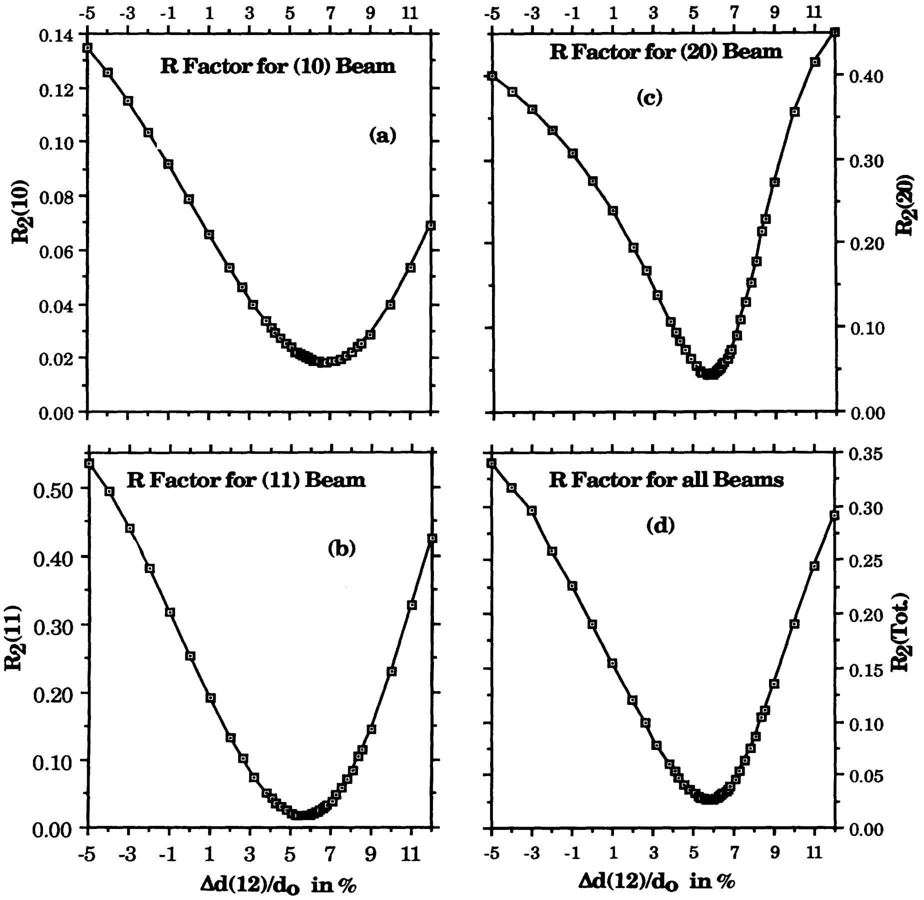

FIG. 1. R_2 values as a function of $\Delta d(12)/d_0$.

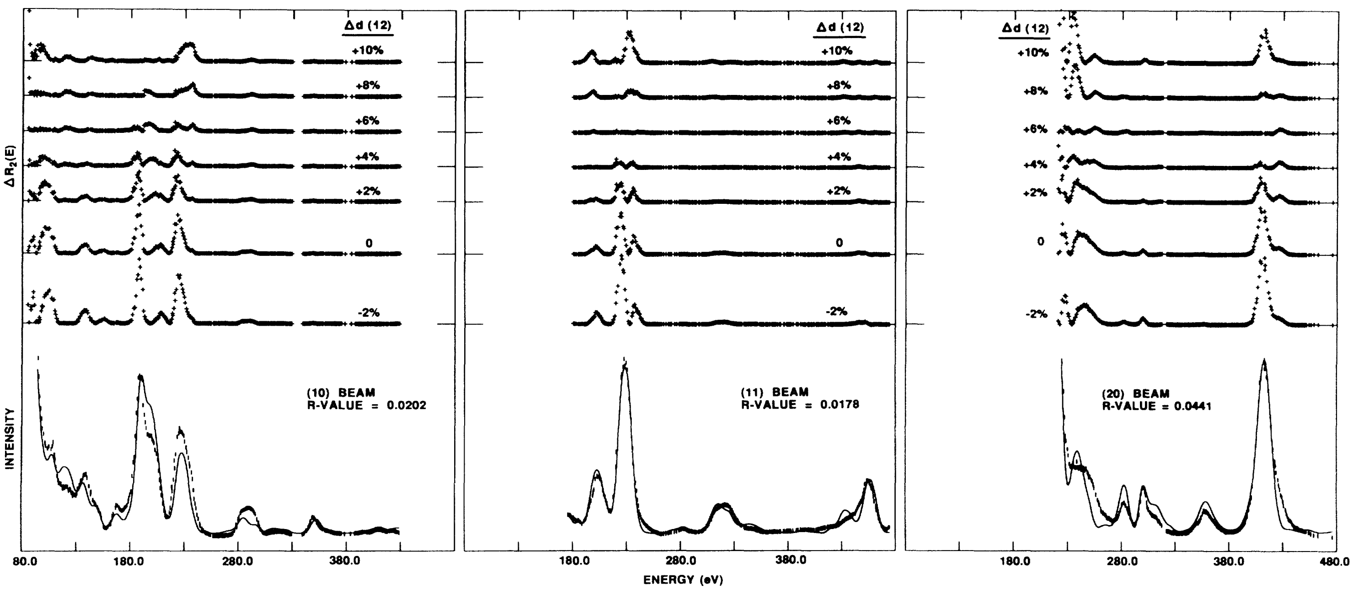

FIG. 2. The experimental (solid) and calculated (dashed) spectra for Be(0001) are at the bottom of the respective subplots. At the top of each subplot are curves of $\Delta R_2(E)$ for various values of $\Delta d(12)$.

analyses. The optimal calculated spectra and the corresponding experimental spectra are displayed in Fig. 2. Above each of the pairs of I-V spectra are curves of ΔR_2 versus incident energy E. Since $R_2 = \sum_E \Delta R_2(E)$, a perfect fit between spectra would produce a straight-line plot for $\Delta R_2(E)$, so it is obvious that the optimal value for $d(12)$ is near 6% expansion.

It was pointed out above that almost all theoretical works predict $d(12)$ contractions, except for the densest faces where (1-2)% expansion might be expected. Thus, an expansion of 5.8% for Be(0001) appears to be anomalous given the fact that most close-packed surfaces show little or no expansion. Perhaps, given the bonding characteristics of Be, this should not be considered surprising. A Be atom has a $2s^2$ configuration which leads to van der Waals bonding in the dimer of 0.1 eV [26]. In the crystal Be forms a very strong (3.32 eV/atom) directional bond due to the hybridization of s and p bands. An explanation of the large $d(12)$ expansion may be contained in theoretical results for Be in isolated planar geometries [27-29]. Mintmire, Sabin, and Trickey [27] using SCLDAC to investigate a single hexagonal layer found that the nearest-neighbor distance was reduced by 3.5% compared to the bulk. Wimmer [28] also investigated the cohesive energy of a hexagonal monolayer by use of SCLDAC. He pointed out that the layer's cohesive energy, compared to the bulk, was anomalously large when compared to other systems. The ratio is 1.5 for Be but only 1.1 for Li [28]. Boettger and Trickey [29] investigated a Be dilayer and found that the in-plane bond length was reduced by ~3% from the bulk. Even more surprising than the in-plane contraction was an interplanar expansion of 5%, which means a c/a ratio of 1.69 for a dilayer compared to 1.57 for bulk and 1.63 for ideal hcp. These results show that the interplanar spacing is greatly influenced by the local atomic coordination. For the semi-infinite surface, the in-plane lattice constant is fixed at the bulk value, and the c/a ratio for a surface with 6% expansion in $d(12)$ is 1.66.

A "universal curve" may be postulated which highlights the apparent anomalous $d(12)$ expansion for Be(0001). Some $d(12)$ results for the simple, noble, and transition metals are plotted in Fig. 3, where $\Delta d(12)/\mathrm{NN}$ is plotted as a function of d_0/NN (NN denotes bulk nearest-neighbor distance). There appears to be an apparent linear dependence of most of the $\Delta d(12)/\mathrm{NN}$ values with d_0/NN. The smaller the value of d_0/NN the more open the surface and the larger the $d(12)$ contraction, which is dominated by the electrostatic attraction caused by surface charge smoothing. For large values of d_0/NN a small $d(12)$ expansion is found for a few surfaces; e.g., the (111) and (100) faces of Al which is a simple metal with a high electron density. In this region of d_0/NN, the sign and magnitude of the relaxation appear to depend upon a critical balance between electrostatic effects and electron screening, which necessitates the need for sophisticated SCLDAC. The solid line in Fig. 3 is the least-squares fit to the observed $d(12)$, with the exclusion of Be and Pb. The dashed lines enclose values within $\pm 2\sigma$. It would be an interesting experimental and/or theoretical task for future work to be able to determine any systematics within the dashed lines. For example, what are the differences between simple and transition metals? Does the screening determine the magnitude of $\Delta d(12)/\mathrm{NN}$ for a given d_0/NN? Be that as it may, Fig. 3 clearly indicates an anomalous $d(12)$ relaxation for Pb(110) and Be(0001).

The LEED results documented above show that

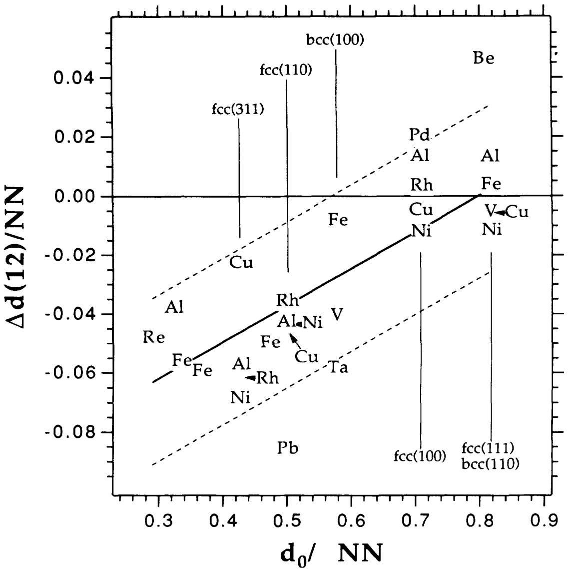

FIG. 3. A comparison of the $\Delta d(12)$/NN as a function of d_0/NN for a wide range of surfaces. The crystal face corresponding to each plotted point is easily obtained from the abscissa value. The points are as follows: Be, this work; Al(111), Ref. [20]; Al(100), J. R. Noonan and H. L. Davis (to be published); Al(110), J. R. Noonan and H. L. Davis, Phys. Rev. B **29**, 4349 (1984); Al(311), J. R. Noonan *et al.*, Surf. Sci. **152/153**, 142 (1985); Al(331), Ref. [3]; Cu(111), S. Å. Lindgren *et al.*, Phys. Rev. B **29**, 576 (1984); Cu(100), Ref. [25]; Cu(110), H. L. Davis *et al.*, Surf. Sci. **83**, 559 (1979); Cu(311), R. W. Streater *et al.*, Surf. Sci. **72**, 744 (1978); Fe(100), K. O. Legg *et al.*, J. Phys. C **10**, 937 (1977); Fe(110), H. D. Shih *et al.*, J. Phys. C **13**, 3801 (1980); Fe(111), H. D. Shih *et al.*, Surf. Sci. **104**, 39 (1981); Fe(211), J. Sokolov *et al.*, J. Phys. C **17**, 371 (1984); Fe(310), J. Sokolov *et al.*, Phys. Rev. B **29**, 5402 (1984); Ni(111), J. E. Demuth *et al.*, Phys. Rev. B **11**, 1460 (1975); Ni(100), W. Oed *et al.*, Surf. Sci. **224**, 179 (1989); Ni(110), S. M. Yalisove *et al.*, Surf. Sci. **171**, 400 (1986); Ni(311), W. T. Moore *et al.*, Surf. Sci. **116**, 253 (1982); Pb(110), U. Breuer *et al.*, Surf. Sci. **239**, L493 (1990); Pd(100), J. Quinn *et al.*, Phys. Rev. B **42**, 11348 (1990); Re(10$\bar{1}$0), H. L. Davis and D. M. Zehner, J. Vac. Sci. Technol. **17**, 190 (1980); Rh(110), W. Nichtl *et al.*, Surf. Sci. **188**, L729 (1987); Rh(100), W. Oed *et al.*, Surf. Sci. **207**, 55 (1988); Rh(311), S. Liepold *et al.*, Surf. Sci. **240**, 81 (1990); Ta(100), A. Titov and W. Moritz, Surf. Sci. **123**, L709 (1982); V(110), D. L. Adams and H. B. Nielsen, Surf. Sci. **107**, 305 (1981) and Surf. Sci. **116**, 598 (1982); V(100), V. Jensen *et al.*, Surf. Sci. **116**, 66 (1982).

Be(0001) has a 5.8% expansion of $d(12)$. This large interplanar expansion should lead to very interesting physical and chemical properties, such as soft phonon modes, two-dimensional electronic properties, and anomalous chemical reactivity.

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[1] For references, see caption to Fig. 3.

[2] Interplanar relaxation is a displacement of one, or more, surface atomic plane which maintains the crystal symmetry parallel to the surface.

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