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Multilayer relaxation of the Mg(0001) surface

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We have investigated the interplanar relaxation of the clean (0001)-(1 × 1) surface of magnesium at 100 K using a dynamical LEED I–V analysis. In contrast to almost all other metal surfaces, an expansion has been observed for the first interlayer spacing of this clean surface. Using an extended database, the results indicate that the first three interlayer spacings are relaxed from the bulk value by \( \Delta d_{12} = +1.9 \pm 0.3\% \), \( \Delta d_{23} = +0.8 \pm 0.4\% \), and \( \Delta d_{34} = -0.4 \pm 0.5\% \). A comparison of this observed multilayer relaxation with experimental and theoretical results for similar free-electron closepacked metal surfaces, e.g. Al(111), suggests that a surface expansion is a normal property of high electron density simple metals.

When a metal crystal is cleaved, a pristine surface is exposed to the vacuum and the minimization of the excess free energy is typically accomplished by structural changes within the surface region. For a few metal surfaces, this involves a mass transport of surface atoms (reconstruction or buckling). However, in most cases the new equilibrium structure is simply associated with displacement of the atomic planes parallel to the surface (relaxation), that is, the interplanar spacings perpendicular to the surface differ from their bulk value. Among the latter category, experimental studies have shown that this relaxation of metal surfaces is characterized by two general trends: (1) The interplanar spacing of the topmost layer is contracted from the bulk value and (2) there is a damped oscillatory relaxation of subsequent layers (multilayer relaxation). Numerous theoretical models have confirmed that these trends are to be expected; that is, contraction is the normal behavior.

However, this “general rule” of contraction is not strictly obeyed. As early as 1970, a jellium based calculation by Lang and Kohn [2] predicted a small expansion (0.5%) of the topmost layer of Al(111); subsequently, three LEED I–V studies have confirmed that the outermost layer is indeed expanded by approximately 1 to 2% [3–5]. Feibelman [6], using a more realistic calculational scheme than employed in the original paper by Lang and Kohn has confirmed that an expansion (1%) of the outermost layer spacing is expected. The magnitude of the expansion of Al(111) is small compared with that observed for beryllium. A dynamical LEED I–V analysis of the Be(0001) surface reports that the outermost layer is anomalously expanded by \(~6\%\) [7]. In agreement with experiment, a recent linearized augmented-plane-wave (LAPW) calculation has correctly predicted a surface expansion (\(~4\%)\) [8]; this study attributes the large expansion to an energy competition between the s → p promotion and the resulting increased bonding at the surface. Because this argument applies predominantly to closed-shell atoms, such as the alkaline-earth metals, it may be expected that the same effects observed for Be will be present on Mg surfaces.

The question we pose is the following: Do the atoms at the surface of a single crystal of Mg behave like the atoms in the bulk (nearly free electron metal) or like the isolated dimer (van der
Table 1
Comparison of various properties of Be, Mg and Al

<table>
<thead>
<tr>
<th>Property</th>
<th>Be</th>
<th>Mg</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimer bond length (Å)</td>
<td>2.46 [34]</td>
<td>3.89 [35]</td>
<td>2.46 [35]</td>
</tr>
<tr>
<td>Dimer binding energy (eV)</td>
<td>0.10 [34]</td>
<td>0.05 [9]</td>
<td>1.89 [36]</td>
</tr>
<tr>
<td>Bulk NN bond length (Å)</td>
<td>2.22 [14]</td>
<td>3.20</td>
<td>2.86</td>
</tr>
<tr>
<td>Bulk cohesive energy per bond (eV)</td>
<td>0.55 [14]</td>
<td>0.25</td>
<td>0.56</td>
</tr>
<tr>
<td>c / a ratio</td>
<td>1.58 [14]</td>
<td>1.62</td>
<td>(\sqrt{8/3})</td>
</tr>
<tr>
<td>Bulk electron density radius(Å)</td>
<td>1.87 [14]</td>
<td>2.65</td>
<td>2.07</td>
</tr>
<tr>
<td>Bulk N(E(_F)) states/eV-atom</td>
<td>0.054 [23]</td>
<td>0.45</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Waals bond? Phrased another way, does Mg behave anomalously like Be and normally like Al?

The Mg atomic ground state configuration, like Be, is a closed-shell [Ne]3s\(^2\). Similar to the noble gases, the electronic stability of the lone atom is reflected in the very small bond strength of the Mg\(_2\) dimer [9] (see table 1). This low value, only a factor of 2 larger than Ar\(_2\) at 300 K [10], suggests a weak van der Waals interaction, that is, the energy cost of 3s \(\rightarrow\) 3p promotion (2.58 eV) [11] is not compensated by the corresponding increase of the electrostatic energy. For comparison, table 1 lists the dimer bond length and binding energy of Al and Be dimers. Mg is more of a van der Waals molecule than Be, and both have a significantly weaker bonding than the Al dimer (0.05 eV compared to 1.9 eV).

The bulk properties of beryllium are anomalous because of the absence of p core electrons. Table 1 shows that Be has a short bond length, a high cohesive energy and a low density of states at the Fermi energy. Mg however, like Al, has structural and electronic properties that are considered "normal" and are typical of nearly free-electron metal. The bulk properties of Mg include a nearly ideal lattice c / a ratio (see table 1). In contrast to beryllium, bulk magnesium and aluminum have a relatively free-electron-like valence band structure. An ab initio pseudopotential calculation [12] indicates there is an approximately equal number of valence 3s and 3p electrons per atom for Mg in the bulk; whereas, Be has a larger percentage of p character [13]. This larger degree of s \(\rightarrow\) p hybridization is responsible for Be having a bulk cohesive energy which is twice as large as Mg and a non-ideal c / a ratio [14]. Although the characteristics of bulk magnesium and aluminum appear quite normal, the properties of Mg in a reduced coordination, unlike Al, are unique.

In two dimensions, an all-electron self-consistent FLAPW calculation [15] predicts that Mg forms the most weakly bound hexagonal self-supporting monolayer of any of the alkaline-earth metals. Due to the small occupation density of p-like valence bands, the Mg monolayer has a small cohesive energy, 0.9 eV, and a nearest-neighbor bond distance that is a factor of 2 larger than the bulk value. In stark contrast, calculations for a single hexagonal layer of Be found that the nearest-neighbor distance was reduced by 3.5% compared to the bulk [16], and the cohesive energy in the monolayer was anomalously large compared to the bulk [15]. Finally, a recent self-consistent calculation [17] demonstrated that, because of the closed nature of the 3s\(^2\) subshell, a Mg atom has no chemisorption minimum on a jellium substrate with an electron density equal to bulk magnesium. This implies that bulk Mg is an unstable metal. Needless to say, the jellium approximation fails in this case; however, it further indicates the unique behavior of the bonding of Mg in lower dimensionality. The bonding coordination number of a Mg(0001) surface atom is only three quarters of that of a bulk atom. Consequently, in this lower-dimensionality environment, the bonding may be considerably weaker than in the bulk, which in turn will affect the equilibrium surface structure.

Thus, comparing the molecular versus bulk properties of Be, Mg, and Al one finds: Both the dimer and bulk of Be have unique properties; and although the dimer of Mg is even more of a real van der Waals molecule than Be, hybridization of the closed shell electrons in the solid makes Mg a free electron metal like Al. At the
surface of Mg, does the reduction in coordination number have a big enough effect to drive Mg back towards the dimer-like properties?

In this article we report the results of a full dynamical LEED $I$–$V$ analysis of the clean Mg(0001)-(1×1) surface at 100 K. Utilizing a large experimental database and a multi-parameter (structural and nonstructural) scattering model, we demonstrate that the stable equilibrium surface structure includes: (1) A multilayer relaxation with a damped-oscillation period which is incommensurate with the lattice and (2) an expansion of the outermost atomic layer from the bulk interplanar spacing value.

The Mg(0001) crystal was cut to within ±0.7° from a single crystal rod and mechanically polished. Upon introduction to the UHV chamber (base pressure $= 5 \times 10^{-11}$ Torr), the sample was cleaned by repeated cycles of sputtering at room temperature with 0.5–1.0 keV Ne⁺ ions and subsequently annealed to 475 K. Sample cleanliness was monitored with HREELS and AES. The LEED pattern at 100 K was quite sharp with low background. The LEED $I$–$V$ data were taken with the sample held at 100 K. The LEED profiles were collected with a video/computer data-acquisition system. The intensity of each spot, normalized to an average background intensity, was recorded by integrating the measured signal within a small window enclosing each spot [18].

All LEED $I$–$V$ spectra were recorded with 1 eV increments at normal incidence.

The hcp (0001) surface has a three-fold symmetry. However, the LEED pattern shows a six-fold symmetry indicating a natural averaging over the two possible terminations (A or B) [7]. The intensity versus energy ($I$–$V$) of each of the inequivalent diffraction beams was determined by averaging the intensity of the symmetrically equivalent spots at each energy point [19]. This “equivalent-beam-averaging” technique helps to reduce both random and systematical errors [20].

The $I$–$V$ profiles of the resulting seven lowest-order inequivalent beams (01), (11), (02), (12), (22), (03), and (04) were recorded and analyzed over an extended energy range.

The experimental $I$–$V$ spectra were then compared to calculated profiles generated from an extensive set of models which included variation of both structural and nonstructural parameters. The calculated spectra were obtained using computer codes [4] based on layer scattering matrices [21] and renormalized forward scattering techniques [22]. To ensure numerical convergence, the dynamical LEED calculations included a 14 layer slab, up to 13 phase shifts, and a sum of spatial lattice points within a circle of ~35 to 40 Å for each atomic layer. The phase shifts were obtained from the Mg potentials tabulated by Moruzzi et al. [23]. $I$–$V$ spectra were calculated and compared to data only within an energy range of 50 to 570 eV.

Based on the symmetry of the observed LEED pattern and the known stability of close-packed surfaces, only structural models which included deviation of interplanar spacings normal to the surface were considered in the calculations. The analysis also included an extensive search of non-structural parameters, i.e., the scattering potential, an energy-dependent complex optical potential, and layer-dependent Debye temperatures ($\theta_D$). These optimal values were determined by comparing the calculated and experimental spectra in terms of a reliability factor ($R$ factor). Although many differently defined $R$ factors exist, an $R_2$ factor [24] was used in this analysis. The total $R_2$ factor is the energy-weighted average of the seven inequivalent beam $R$ factors.

The optimal model parameters were achieved when the normalized mean-square difference ($\sim R_2$) between the experimental and calculational profiles was minimized. This specific analysis entailed approximately 950 iterative cycles of both structural and nonstructural parameters before a minimal total $R_2$ factor was obtained and, correspondingly, before the optimal values of interlayer spacings near the surface were determined.

Fig. 1 illustrates the variation of the total $R_2$ factor as a function of the difference in the interplanar spacing between the first two layers ($\Delta d_{12}$). $\Delta d_{ij}$ is defined as $(d_{ij} - d_0)/d_0$, where $d_0$ is equal to the bulk interplanar spacing ($d_0 = 2.61$ Å) and $d_{ij}$ is the distance between the $i$th and $j$th crystal plane from the surface. There is a smooth minimum in $R_2$ corresponding to an expansion ($\Delta d > 0$) of the first atomic layer. The
reliability factor minimum was found by an iterative process of varying the interplanar spacings followed by varying of nonstructural components. This cycle was repeated until the final minimal \( R_2 = 0.0184 \) was found. In fig. 2, experimental (EXP) \( I-V \) spectra (dotted lines) are shown for the seven beams used in the calculation. The solid lines correspond to the calculated (CAL) \( I-V \) spectra using the best model parameters determined from the minimal \( R_2 \). Visually, it is evident that the differences between CAL and EXP are mainly in small intensity differences, that is, the peak positions and widths coincide well.

Values of optimized model parameters are shown in table 2. The results of this analysis indicate a multilayer relaxation at the Mg(0001) surface and an expansion of the first two interlayer spacings. Note that the determined interplanar relaxations do not follow an oscillatory behavior which is commensurate with the lattice. The magnitudes of the calculated errors (\( \pm \Delta d_{ij} \)'s) were determined from extensive variations of the parameters and reflect the small total \( R_2 \) value of this analysis. To our knowledge, this \( R_2 \) factor is the lowest value for any LEED \( I-V \) study in the literature; in comparison, the minimal \( R_2 \) achieved was 0.0191 for Al(111) [4] and 0.0261 for Be(0001) [7]. The combination of this low \( R \)-factor and the extensive database provides confidence in our determined \( \Delta d_{ij} \) values.

Similar to other LEED \( I-V \) studies that include layer-dependent Debye temperatures [4,25], the optimal \( \theta_D \) of the outermost layers are substantially lower than the determined “bulk” value (see table 2). The explanation of this observed phenomenon is that the atomic forces near the surface are softer; consequently, the thermal vibrations in the top layers are greater than that of the bulk. However, the determined “bulk” value, 520 K, is well above the bulk Debye temperature of magnesium as measured in X-ray experiments (406 K). The origin of this apparent discrepancy lies in the “blurred atom” model used in the LEED analysis. Not only does this model assume an isotropic and a harmonic atomic motion, it neglects long-range, correlated motion between neighboring atoms [21]. This type of discrepancy was also observed in dynamical LEED \( I-V \) calculations of both Al(111) [4] and Be(0001) [7].

Landman et al. [26] have been pointed out that the existence of multilayer \( \Delta d_{ij} \) oscillations is a natural extension of the point-ion electrostatic model of surface relaxations first proposed by Finnis and Heine [27]. With the inclusion of a realistic three-dimensional charge density at the surface and with the proper evaluation of the screening of the conduction electrons, Barnett et al. [28] have shown that the period of the multilayer oscillations may not be commensurate with the lattice. Eguiluz [29] has extended this “dielectric screening” model within a self-consistent linear-density-response LDA formalism and has shown that the multilayer oscillation period is associated with the Fermi wave vector \( k_F \). Our results (see table 2) show that, the period of interlayer oscillation is not equal to that of the lattice. If a plot of the experimentally determined \( \Delta d_{ij} \)’s versus lattice plane is fitted with a damped sinusoidal function, the oscillation period is \( \sim 8.3 \) Å. This corresponds to a distance which is within 10% of either \( 3d_0 \) or \( 2d_F \). Because calculational uncertainties of the deeper \( \Delta d_{ij} \)'s are relatively large, the determined period is only an estimation and should not be viewed as a confirmation of any specific theoretical prediction.
Fig. 2. $I$-$V$ spectra for seven LEED beams of Mg(0001) at 100 K. The experimentally measured spectra are compared to the calculated spectra that produce the best agreement for the total $R$. Single beam $R$ are given to quantify the quality of agreement for each beam.
To directly compare the determined expansion of this system with Al(111) and Be(0001), it is necessary to normalize the respective $\Delta d_{12}$'s by the bulk nearest-neighbor (NN) distance. Detailed LEED studies have shown that $\Delta d_{12}/NN$ for these close-packed faces are: Be = +4.7% [7]; Al = +1.4% [4] or +0.7% [3]; and for this work Mg = +1.5 ± 0.2%. As can be seen, Be has an anomalously large expansion. However, the very similar magnitudes of Mg and Al imply that the driving force of the surface expansion may be the same. Potassium, another free-electron metal, exhibits a 0.7% contraction [30], which may be a consequence of its low bulk-electron density ($r_s$ = 4.86 a.u.). These observations suggest that there is an increasing propensity of outerlayer expansions of simple metal surfaces with increasing substrate electron density (decreasing $r_s$).

There have been a number of theoretical investigations which predict the $\Delta d_{12}$ at the Mg(0001) surface. As alluded to in our introduction, one study [17] has shown that there is no chemisorption minimum for the Mg/jellium ($r_s = 2.65$ a.u.) system. However, by including the effects of the lattice, using weak pseudopotentials in lowest-order perturbation theory, this self-consistent calculation predicts a weak chemisorbed bond (0.5 eV) with a predicted equilibrium distance (atop site) slightly below the observed dimer bond length (3.89 Å) [9]. This type of calculational scheme has recently been extended by modelling the interatomic interactions within an effective-medium theory (EMT) [31] and has predicted equilibrium interplanar contraction of 1%.

Using an approach similar to the embedded-atom method (EAM), Chen [32] has also reported the interplanar relaxations of a variety of hcp metals utilizing local volume potentials (LVP). This study finds that the outermost plane of Mg contracts by 0.4%. In contrast to these results, a very recent plane-wave pseudopotential calculation finds an expansion of 1.5% [33]. A comparison of the results of these theoretical studies with our experimental data is shown in table 3.

### Table 2
LEED $I-V$ optimized parameters ($d_0 = 2.61$ Å)

<table>
<thead>
<tr>
<th>Layer</th>
<th>Interlayer spacing (in %)</th>
<th>Debye temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\Delta d_{12} = +1.9 \pm 0.3$</td>
<td>260</td>
</tr>
<tr>
<td>2</td>
<td>$\Delta d_{23} = +0.8 \pm 0.4$</td>
<td>380</td>
</tr>
<tr>
<td>3</td>
<td>$\Delta d_{34} = -0.4 \pm 0.5$</td>
<td>520</td>
</tr>
<tr>
<td>4</td>
<td>$\Delta d_{45} = +0.0 \pm 0.5$</td>
<td>520</td>
</tr>
</tbody>
</table>

### Table 3
Multilayer relaxation: comparison between the experimental and theoretical results

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\Delta d_{12}$ (in %)</th>
<th>$\Delta d_{23}$ (in %)</th>
<th>$\Delta d_{34}$ (in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>+1.9</td>
<td>+0.8</td>
<td>-0.4</td>
</tr>
<tr>
<td>Theory</td>
<td>+1.5</td>
<td>+0.5</td>
<td>+0.1</td>
</tr>
<tr>
<td></td>
<td>-1.0</td>
<td>-0.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-0.39</td>
<td>-0.27</td>
<td>-0.29</td>
</tr>
<tr>
<td>This work</td>
<td></td>
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<tr>
<td>[33]</td>
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<tr>
<td>[31]</td>
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<td>[32]</td>
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</tbody>
</table>
It is not known whether the “electron promotion” argument adequately explains the expansion of Mg and Al close-packed surfaces, although it reasonably accounts for the anomalous relaxation results of Be(0001) [8]. This is not surprising in light of the many abnormal properties of beryllium caused by the lack of p core-electrons, a feature not shared by either magnesium or aluminum. Because of the similarities between these latter two simple metals, the observed surface expansions indicate that the spatial variation of the charge density of the free-electron surface may cause the effect. In order to verify this, it would be interesting to investigate the surface relaxation as a function of the metal’s $r_e$ and crystallographic face. This additional evidence may support the assertion that the expansion of Mg(0001) is a normal effect of a metal surface.

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References

[13] This calculation also predicts a small anisotropy in the different $p$ components of bulk Be; that is, $p_x \geq p_z$. $p_y$ ($\hat{z}$ is perpendicular to the basal plane). This fact is consistent with the non-ideal $c/\alpha$ ratio.
[19] For example, the $I-V$ curve for the (01) beam was determined by averaging the $I-V$ profiles of the (00), (11), (00), (11), and (01) beams.