I. INTRODUCTION

Characteristic of group-V elements, bismuth crystallizes in the rhombohedral $A\overline{7}$ structure as a semimetal with a small density of states at the Fermi level. But interestingly, the surfaces of Bi show very different electronic properties from the bulk. Studies on the Bi(110), Bi(100), and Bi(111) surfaces have shown that they are much more metallic than the bulk due to a significantly higher density of states at the Fermi level at the surface. It has been found that one significant contribution is from a strong spin-orbit coupling at the surface due to broken inversion symmetry.

From a chemical point of view, the creation of a surface requires the breaking of atomic bonds. Covalent bonding plays only a minor role in most metals. Thus the effect of bond breaking is small and surface properties are similar to those of the bulk, although localized electronic surface states may be present. On semiconductors, creating a surface leaves dangling bonds which should give rise to half-filled density of states at the Fermi level. However, it turns out that on most semiconductor surfaces the atoms rearrange their positions such that the dangling bonds are removed and the surface is again a semiconductor and not a metal. Semimetals such as bismuth lie in between these two cases. On one hand, a semimetal is close to being a semiconductor since directional bonding is important and the valence and conduction bands are almost separated by a gap. On the other hand, there is a very small overlap between both bands such that the material is formally a metal. This delicate balance between being a metal and a semiconductor depends crucially on the atomic structure and it can be expected to be severely disturbed at the surface.

Detailed structural information on Bi surfaces is so far limited to a recent low-energy electron diffraction (LEED) intensity vs voltage (IV) and first-principles study of the Bi(111) surface. One important difference between bulk-terminated Bi(110) and Bi(111) is that the Bi(110) surface exhibits dangling bonds, while Bi(111) does not. In a pioneering study by Jona, oxygen adsorption experiments suggest that Bi(110) is noticeably more active than Bi(111). A qualitative analysis of LEED patterns in Jona’s study shows an unreconstructed (1 × 1) Bi(110) surface structure. From the bulk structure Jona erroneously concluded that the unit cell (and hence the LEED pattern) should not be exactly rectangular but that the lattice vectors should include an angle slightly different from 90°. This is not correct, as will become apparent below. The unit cell is rectangular and almost square. A recent scanning tunneling microscopy study by Pascual et al. revealed images of the Bi(110) surface that are consistent with a near-square surface unit cell.

In contrast to most metal surfaces, Bi(110) has a very low symmetry—the only symmetry element being a mirror plane while it has no translational symmetry normal to the surface. This makes the LEED IV analysis of this surface challenging. Along the [110] direction the Bi has a close stacking of atomic layers, i.e., the buckled bilayer as described below that requires the combined space method to calculate diffraction matrices. The stacked layers have a registry that does not repeat itself, or in other words, the stacking sequence has an infinite repeat distance due to its nonsymmetrical translation parallel to the mirror plane. More importantly, the dangling bonds at the surface may complicate the surface electronic and geometrical structures, which makes this open surface quite similar to many semiconductors and binary compounds.
II. BULK TRUNCATED Bi(110) SURFACE STRUCTURE

The A7 (α-arisenic) structure of bulk bismuth has a rhombohedral unit cell with a two-atom basis. This structure can be obtained by a slight stretching of two penetrating face-centered cubic structures along the body diagonal. The bulk truncated surface structure of Bi(110) is shown in Fig. 1.

Each atom has three nearest neighbors to which it is connected by quasicovalent bonds. The side views show the stacked bilayers loosely bound by a single bond between every other atom in neighboring bilayers. Within one bilayer, each atom in one layer closely bonds with two nearest-neighbor atoms in the other layer, forming a buckled structure. The covalent bonds have been drawn by solid lines and the dangling bonds at the surface layer by dashed lines. The bilayer-type structure gives rise to alternating interlayer distances. For the truncated bulk at 110 K we have $d_{12}^\perp = 0.208 \, \text{Å}$, $d_{13}^\perp = 3.064 \, \text{Å}$, $d_{14}^\perp = 0.208 \, \text{Å}$, $d_{15}^\perp = 3.064 \, \text{Å}$, and so on. Interlayer spacings between the $i$th and $j$th bulk layers are indicated as $d_{ij}^\perp$. Noticeably, the Bi(110) surface has very low symmetry: the only symmetry element is a mirror plane as indicated in Fig. 1. The lengths of unit vectors at 110 K are taken as 4.731 and 4.538 Å; see Refs. 12, 14, and 15. If the rhombohedral structure is treated as a pseudocubic structure as in Ref. 12, Bi(110) will be denoted as Bi(100). The pseudosquare character of the surface unit cell is evident: for a cubic Bi structure all the atoms in the first bilayer would have the same height, the unit cell would be rotated by about 45°, and contains only one atom.
In the LEED intensity analysis, agreement between experimental and calculated LEED intensities is quantified by the widely used Pendry $R$ factor $R_p$, which is particularly sensitive to relative peak position and the existence of small peaks. The uncertainties in the optimized structural parameters are estimated from the variation around the minimum $R_{p\min}$,

$$
\Delta R_p = R_{p\min} \times \sqrt{\frac{V_{in}}{\Delta E}},
$$

where $\Delta E$ is the total energy range compared in the IV analysis.\(^{19}\)

C. Ab initio calculations

We have also performed ab initio calculations of the surface crystal structure of Bi(110). The full-potential linearized augmented plane wave method in film geometry\(^{20,21}\) as implemented in the FLEUR code was used and the local density approximation\(^{22}\) to the density functional theory was employed. Spin-orbit coupling was included in the self-consistent calculations.\(^{23}\) The evaluation of the surface relaxation has been carried out for the symmetric 14-layer film, both with the inclusion of the spin-orbit coupling (SOC) term and without this term. Force calculations have been performed for the first four layers without spin-orbit coupling while relaxations have been carried out only for the first two interlayer spacings with the inclusion of SOC. In the latter evaluations we kept the interlayer spacings $d_{sl}$ and $d_{sl}$ equal to those obtained from the force calculation without SOC. The geometry was chosen such that both sides of the film were terminated with an intact bilayer. A wave-function cutoff of 3.8 a.u.$^{-1}$ was chosen and the Brillouin zone was sampled with 32 $k$ points.

IV. RESULTS AND DISCUSSIONS

A. LEED structure determination

The LEED pattern of Bi(110) has previously been discussed by Jona.\(^{12}\) He defined a pseudocubic bulk unit cell and concluded that the unit cell (and hence the LEED pattern) should not be exactly rectangular but that the lattice vectors should include an angle slightly different from 90°. Our study does not confirm this conclusion. Our LEED patterns as presented in Fig. 2 show an exact rectangular net from careful measurements of the diffraction spots positions and, indeed, such an exact rectangle can also be expected from a projection of the bulk reciprocal lattice onto the surface.\(^{6}\) The measured ratio of the two reciprocal unit cell vectors is 0.96(2) in good agreement with the expected value of 0.959. Moreover, the observed patterns show no indication of any reconstruction of the Bi(110) surface, despite the existence of active dangling bond at the surface. Apparently, Bi(110) is found to be very different from typical semiconductor surfaces, such as Si(100) and Ge(100) which both exhibit 2×1 reconstructions.

The structural and nonstructural parameters were optimized for a Bi(110) surface terminated by an intact bilayer. A termination with a split bilayer was immediately excluded due to lack of agreement with the experimental IV curves.
shown in Figs. 3 and 4, 20 symmetry inequivalent beams with a total energy range of 3591 eV have been analyzed to determine the following structural and nonstructural parameters: the first four interlayer spacings $d_{ij}$ ($j=i+1; 1 \leq i \leq 4$), the real part of the inner potential $V_0$, and Debye temperatures $\Theta_{D_1}$ and $\Theta_{D_2}$ for atoms in the first and second layers, respectively. The results of the structural analysis are summarized in Table I. Note that the first and the third interlayer
spacings correspond to the small separation (0.21 Å) between the two layers making up the bilayer in the bulk. Their seemingly dramatic relative relaxations are very small in absolute terms. Also, the fourth layer appears to move above the third layer by 0.01 Å. However, this very small value is clearly below our detection limit. Overall no significant relaxation for the Bi(110) surface is found. We have tried many possible displacement patterns allowed due to the low surface symmetry. However, we found no significant improvement in $R_P$ when changing the relative distance between the
two basis atoms in the first and second layers parallel to the mirror line. The Debye temperature for the first layer is found to be lower than that of the bulk, which is consistent with an early study of Goodman and Somorjai. Reduced surface Debye temperatures are a common phenomenon reflecting the weaker bonding of surface atoms compared to the bulk. The actual numerical values of the surface Debye temperature are an important ingredient for the determination of the electron-phonon coupling strength from angle-resolved photoemission data. Meanwhile the second layer shows a Debye temperature close to the bulk value.

The LEED IV analysis gives a relatively high \( R_p \) factor of about 0.455 compared to typical values of 0.1 to 0.3 for clean unreconstructed metal surfaces. Many efforts have been made to find out the possible causes. We simulated non-normal-incidence conditions extensively in the LEED IV calculations and found that an increase in the incident angle gave a dramatic rise in the \( R_p \) factor from its minimum at zero or normal incidence. This suggests that the sample is properly aligned and the relatively high value is not caused by deviations from normal incidence during the IV measurement. The influence of the muffin-tin radius on the structure has been studied and results show essentially the same geometry with a minimum \( R_p \) factor at 2.87 a.u. We also tried the atomic potential derived from our \textit{ab initio} calculations with no significance changes in the optimized structural parameters nor an improvement in the \( R_p \) factor. So it might be the structural complexity and low symmetry of \( \text{Bi}(110) \) itself that complicates the LEED process. As seen on open semiconductor surfaces, the presence of dangling bonds and the presence of voids in the open surface structure is a real challenge for the muffin-tin approximation of the crystal potential and could also contribute to the relatively high \( R_p \) for this surface. However, the low surface symmetry of \( \text{Bi}(110) \) gives rise to the large number of nonequivalent beams. Here we present an accumulative energy range of 3591 eV (20 beams) which is larger than about 1000 eV used in typical LEED studies. When an overall range of only 1071 eV (the first six beams) was analyzed in our work, the \( R_p \) factor decreased to 0.36 without changes in the optimized structural parameters. This value is comparable to LEED results for many semiconductors and

![FIG. 5. (Color online) Error bar determination for the first four interlayer spacings based on \( \Delta R_p = 0.043 \) and Eq. (2).]
metal oxide compounds with similar geometric and electronic structures. Interestingly, the reduction of $R$ factor due to fewer beams indicates more intricate scatterings in the higher ordered beams. Furthermore, with horizontal surface atomic displacement in the mirror plane allowed, a smaller $R$ has been obtained but, considering that the displacement values are within error limit and no significant geometry change occurred, we are not including these displacements in the report. The agreement between this large experimental data set and the calculated intensity-energy curves, as shown in Figs. 3 and 4, gives us confidence in the reliability of our results.

The error bars of the optimized parameters were analyzed based on the variation of the $R$ factor around $R_{p_{\text{min}}}=0.043$ according to Eq. (2). The dependence of $R_p$ on a change of the interlayer spacings away from their optimized values is shown in Fig. 5. In this analysis, all other parameters were fixed at their optimized values. We can see that all the sensitivity curves take on a parabolic shape. The errors for the individual parameters are also listed in Table I.

**B. Comparison to first-principles calculations**

The first-principles calculations performed for bulk Bi without the inclusion of spin-orbit interaction give bulk short and long interlayer spacings of 0.142 and 3.087 Å, respectively. Evaluations that include the SOC term lead to a very good agreement with those obtained by the LEED IV curves. No structural reconstruction occurs despite of dangling bonds present at the surface. No significant absolute value of relaxation is found for the first four interlayer spacings. The reduced top-layer Debye temperature suggests essentially larger vibrational atomic amplitudes at the surface. Experimentally, the approach of sample alignment by calculating the diffraction spot positions on the LEED screen is very efficient and can be used for surfaces with low symmetry as well as for insitu cleaved surfaces.

**V. Conclusions**

Our results give a consistent picture of the very low-symmetry surface geometric structure of Bi(110) by LEED intensity analysis and first-principles calculations. Good agreement is reached between experimental LEED and theoretical IV curves. No structural reconstruction occurs despite of dangling bonds present at the surface. No significant absolute value of relaxation is found for the first four interlayer spacings. The reduced top-layer Debye temperature suggests essentially larger vibrational atomic amplitudes at the surface. Experimentally, the approach of sample alignment by calculating the diffraction spot positions on the LEED screen is very efficient and can be used for surfaces with low symmetry as well as for in-situ cleaved surfaces.

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