The effect of reduced dimensionality on a semimetal: the electronic structure of the Bi(110) surface

S Agergaard\textsuperscript{1}, Ch Søndergaard\textsuperscript{1}, H Li\textsuperscript{1,2}, M B Nielsen\textsuperscript{1}, S V Hoffmann\textsuperscript{1}, Z Li\textsuperscript{1} and Ph Hofmann\textsuperscript{1}

\textsuperscript{1} Institute for Storage Ring Facilities, University of Aarhus, DK-8000 Aarhus C, Denmark
\textsuperscript{2} Department of Physics, Zhejiang University, Hangzhou 310027, China

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Abstract. We have studied the electronic structure of the semimetal surface Bi(110) by high-resolution angle-resolved photoemission using synchrotron radiation. Several surface states are found very close to the Fermi level giving rise to a complex Fermi surface. As a consequence, the surface is a much better metal than the bulk, a fact which could help to explain the observation of superconductivity in granular systems built from small Bi clusters.

One of the most fascinating aspects in the study of surfaces is the effect of reduced dimensionality on the geometric and electronic structure. The creation of a surface requires the breaking of atomic bonds. In most metals, covalent bonding plays only a minor role. The effect of bond-breaking is small and the surface properties are similar to those of the bulk, although localized electronic surface states may be present. On semiconductors, creating the surface leaves so-called dangling bonds which should give rise to half-filled and therefore metallic bands. However, it turns out that on most semiconductor surfaces the atoms re-arrange their positions such that the dangling bonds are removed and the surface is again a semiconductor, not a metal. Semimetals 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, a very small overlap between both bands is found at some point of the Brillouin zone such that the material is formally a metal. This delicate balance between being a metal and a semiconductor depends crucially on the structural details \cite{1} and is disturbed severely at the surface. A semimetal surface can be expected to turn either into a better metal or into a semiconductor. The former case is more interesting because a good metallic surface...
on a semimetal (or, indeed, on a semiconductor) can be taken as a model for a nearly two-dimensional metal. Metallic surfaces have been found on Be [2, 3] and α-Ga [4]. In both cases directional bonding is important and the bulk density of states has a minimum at the Fermi level, even though the absolute value is much higher than in a ‘traditional’ semimetal such as Sb, Bi or As.

Recently, the possibility of finding metallic surface states on rhombohedral Bi clusters has attracted some attention. Weitzel and Micklitz have shown that granular systems built from such clusters show superconductivity at rather high temperatures (up to several K) [5] while pure rhombohedral bulk Bi is not a superconductor down to very low temperatures [6]. A possible explanation of these findings is an enhanced density of states (DOS) at the Fermi level in the clusters which would favour the transition to the superconducting state. The dependence of the transition temperature on the cluster size suggests that electronic states on the cluster surfaces might be responsible for a high DOS at the Fermi level. In photoemission studies, which have been restricted to the close-packed Bi(111) surface, no genuine metallic surface states have been found so far [7]–[10]. However, there is strong evidence that the bulk electronic structure is severely modified close to the surface, rendering it more metallic than the bulk [11].

The Bi(110) surface is a much better candidate for finding a metallic surface state because the truncated bulk structure supports a dangling bond state on every other surface atom[12]. In this paper we show that Bi(110) is indeed a good metal with a rather complex surface Fermi line. We also point out that this metal might have rather peculiar properties because of the large spin–orbit splitting in Bi, which is likely to cause the surface state bands to contain only one electron per $\vec{k}_\parallel$ point.

Before explaining the experimental details, it is worthwhile to look at the general properties of the Bi(110) surface, both in real and in reciprocal space. The geometrical properties of a rhombohedral arsenic-type (110) surface have been discussed in a pioneering work by Jona [12]. We will just highlight some points of particular relevance here. The first thing to notice is the fact that while the real Bi structure is rhombohedral, it may also be described as pseudo-cubic or hexagonal. Bi(110) is a pseudo-cubic (100) surface and a hexagonal (0112) surface. Figure 1 shows the real space structure of the truncated bulk Bi(110) surface together with the surface unit cell which contains two atoms. Note that we define a smaller unit cell than Jona [12]. The two real space lattice vectors enclose a right angle and are almost equal in length. The surface has a very low symmetry. The only symmetry element is a mirror line which is also indicated in the figure.

Figure 2 shows the bulk Brillouin zone (BZ) of Bi and its projection on the (110) surface. We call the points at the sides of the surface Brillouin zone (SBZ) $\bar{X}$ and the points at the corners $\bar{M}$. Like the real space unit cell, the SBZ has only one mirror line, labelled $m$ in figure 2(b). This low symmetry is reflected in the electronic structure. For example, the $\bar{X}_2$ and $\bar{X}_2'$ points correspond to $k_\perp$ rods along the $T$–$L$–$T$ line of the bulk BZ but the $\bar{X}_1$ points correspond to a $k_\perp$ rod along the $L$–$L$–$L$ line. This means that the projection of the bulk electronic structure at $\bar{X}_2$ and $\bar{X}_2'$ is different from that at $\bar{X}_1$. The bulk BZ in figure 2 also contains a sketch of the bulk Fermi surface. It consists of electron pockets at the L points and hole pockets at the T points. A projection of this Fermi surface on the (110) surface results only in features in the immediate vicinity of the four $\bar{X}$ points.

The presence of only one mirror plane in the SBZ might lead to the conclusion that the dispersion of the electronic surface states in the left half of the SBZ in figure 2(b) could be different from that in the right half. This is, however, not the case because of time-reversal symmetry.

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For a two-dimensional system it leads to a symmetry in the dispersion of the electronic states

\[ E(k_\parallel, \uparrow) = E(-k_\parallel, \downarrow). \]  

(1)

This means that if one has a surface state at \( k_\parallel \) with a binding energy \( E \) and a spin \( \uparrow \), then there must also be a state at \( -k_\parallel \) with the same energy but spin \( \downarrow \). To see the consequences of this more clearly, consider for example the lower \( \bar{M}_1 \) point in figure 2(b). Time-reversal symmetry causes the upper \( \bar{M}_2 \) point to have the same electronic structure and the application of mirror symmetry renders all \( \bar{M} \) points equivalent. In other words, the combination of time-reversal and mirror symmetry has the consequence that the surface state dispersion is also symmetric with respect to the line which is perpendicular to \( m \) (the line labelled \( m_2 \) in figure 2(b)). In addition to the fact that all \( \bar{M} \) points become equivalent, it is sufficient to measure the electronic states in a quarter of the SBZ. All this is only true if spin is not an issue, like in our non-spin-resolved experiment.

The Bi crystal was mechanically polished within 0.5° of the (110) surface. The orientation of the bulk mirror plane was determined by Laue diffraction such that the \( \bar{X}_1 \) and \( \bar{X}_2 \) points could

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Figure 2. (a) The bulk Brillouin zone of Bi and the projection on the (110) surface. A sketch of the bulk Fermi surface is included (not to scale). (b) the surface Brillouin zone in detail. The only symmetry element is the mirror line $m$. The line $m_2$ is an effective second mirror line for the surface state dispersion caused by the combination of the real mirror line and the time-reversal symmetry (see text).
be identified later in the photoemission experiments. After insertion into the vacuum system, the surface was cleaned by cycles of Ar and Ne sputtering and annealing. In the first stages of the cleaning, the annealing temperature was chosen to be 200 °C, later 50 °C was found to be sufficient, consistent with the fact that Bi has a very low Debye temperature (119 K). Surface order was checked by low energy electron diffraction (LEED) and cleanliness by photoemission. The surface was found to exhibit a fair quality \((1 \times 1)\) LEED pattern, in agreement with the work of Jona [12]. The photoemission experiments were performed using an angle-resolved electron spectrometer at the SGM-3 beamline on the undulator of the storage ring ASTRID in Aarhus. A detailed description of the instrument will be given elsewhere [13]. In short, the beamline covers an energy range from 12 eV to 140 eV with a resolving power better than 15 000. For the measurements reported here, the light was incident under an angle of 50° away from the surface normal with the polarization vector of the light coinciding with the mirror plane of the crystal. Alternatively, a discharge lamp was used to produce unpolarized He I radiation. The electron spectrometer is a commercial VG ARUPS 10 analyser which is mounted on a goniometer inside the chamber and equipped with a multichannel detector. The analyser position can be changed by motors outside the chamber. The total energy resolution used in this work was better than 30 meV for the surface state dispersion measurements and around 50 meV for the Fermi line mapping. The angular resolution was around ±0.7°. The sample temperature was around 30 K.

We have measured the dispersion of the electronic states in the entire lower half of the SBZ shown in figure 2. The upper part cannot be reached by the electron analyser. In agreement with the reasoning given above, the dispersion of the surface states was found to be symmetric with respect to the \(m_2\) line in figure 2. Therefore, we only report the electronic dispersion in a quarter of the SBZ in the following.

Figure 3 gives the main results of this study. It shows a projected band structure of Bi(110) along the main symmetry lines in the region of the p-bands together with the measured surface state dispersion. The projected band structure was calculated using the tight-binding parameters determined by Liu and Allen [14]. These authors have carefully tuned the parameters such that the calculated band structure is in good agreement with the measured bulk Fermi surface. Therefore we expect the projection to be rather accurate on the energy scale we are interested in here. The surface states have been identified by the fact that they appear as sharp peaks, their position in a projected bulk band gap and the fact that they do not show dispersion upon changing \(k_\perp\) via the photon energy. For the reader interested in the raw data, two of the photoemission spectra used to create the grey-scale plot in figure 3 are shown in figure 4.

We can clearly identify several surface states (A, B, C, D, E) in figure 3. All of them except state E give rise to a fraction of the surface Fermi line. The states A and B form hole pockets around the \(\bar{\Gamma}\) and \(\bar{M}_1\) points, respectively. The effective mass of both states can be estimated to be of the order of one electron mass. This is in sharp contrast to bulk Bi where the effective masses of the carriers are very small in most directions, contributing to the low density of states at the Fermi level. The state C forms an electron pocket around the \(\bar{M}_1\)–\(\bar{X}_1\) line. For the state D the situation is less clear. It seems to cross the Fermi level only in the \(\bar{X}_1\)–\(\bar{\Gamma}\) direction.

We have investigated the shape of the surface Fermi line more closely by measuring the intensity at the Fermi edge as a function of \(k_\parallel\) at different photon energies. Figure 5 shows the result of such a measurement for a photon energy of 16 eV. At other energies the intensity ratio between the surface-related Fermi lines changes but the images look qualitatively the same. Figure 5 displays the raw data, i.e. the integrated photoemission intensity of a 50 meV wide

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Figure 3. Projected band structure and experimental data along several high symmetry lines of the surface Brilloin zone. The data give the logarithm of the photoemission intensity taken at $h\nu = 16$ eV. The grey scale is defined such that black means low intensity and white high intensity. The features A, B, C, D and E are the electronic surface states discussed in the text. The two arrows denote the $\vec{k}_\parallel$ points for which photoemission spectra are shown in figure 4.

window centred on the Fermi level. The hole pockets created by the states A and B in figure 3 are clearly visible and so is the small electron pocket from state C. The state D merely gives rise to a weak intensity along the $\bar{X}_1-\bar{\Gamma}$ line. In addition to these surface-related features we find a maximum close to $\bar{X}'_2$ which is probably caused by bulk Fermi level crossing.

The most important consequence of these findings is that Bi(110) is very different from bulk Bi. It has a complex surface Fermi line consisting of two hole pockets around $\bar{\Gamma}$ and $\bar{M}_1$, an electron pocket along the $\bar{M}_1-\bar{X}_1$ line and a feature close to the $\bar{X}_1-\bar{\Gamma}$ line. The effective masses for the two hole pockets are of the order of a free electron mass, much higher than for most bulk carriers, such that the surface is a better metal than the bulk.

It is interesting to speculate about the nature of the surface states. Unfortunately, the geometric structure of Bi(110) is not known apart from the fact that the LEED pattern is $(1 \times 1)$. It seems likely, however, that the surface states are related to the dangling bond situated on one atom in the surface unit cell as discussed by Jona [12] (see figure 1). The density of dangling bonds is relatively low and not sufficient to induce a reconstruction like on many semiconductor surfaces. It has to be pointed out, however, that in the present case a $(1 \times 1)$ LEED pattern still leaves ample room for atomic re-arrangements which can lower the total energy without affecting the periodicity parallel to the surface. This is because of the fact that there are two atoms in the surface unit cell. A re-hybridization which just changes the position of the white atom within the surface unit cell of figure 1, for example, would not change the LEED pattern.

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A quantitative LEED study could clarify this.

Another noteworthy point is that the surface state bands are likely to be completely non-degenerate, i.e. for every \( \vec{k}_\parallel \) point, only one electron can be found in a band. This is caused by the combination of spin–orbit splitting and the symmetry loss at the surface. In bulk Bi, spin–orbit splitting has a considerable effect on the band structure due to the large spin–orbit coupling parameter \( \lambda \) which is about 1.5 eV [14]. The spin–orbit interaction changes the dispersion of the bands but it does not remove the two-fold spin degeneracy because of the inversion symmetry in the bulk structure [15]. At the surface, the bulk inversion symmetry is broken and a complete lifting of the degeneracy can be expected. Spin–orbit split surface states have, in fact, already been observed on Au(111) [16, 17], Mo(110) [18] and W(110) [18]. Here, we can expect the spin–orbit splitting to be so large that only one of the split bands is observable. Alternatively, it is also possible that the pairs of states which we observe at several points in the SBZ (e.g. B and C or A and D) correspond to the same states separated by the spin–orbit splitting.

A non-degeneracy of the surface state bands has interesting consequences. Consider, for example, the hole pocket around the \( \bar{\Gamma} \) point. If we take an electronic state on this Fermi line with a wave-vector \( \vec{k}_\parallel \) and a certain spin then the electron with \( -\vec{k}_\parallel \) will have a spin in the opposite direction. This will affect the screening properties of this electronic system. In a normal,
Figure 5. Integrated Fermi level intensity for $h\nu = 16$ eV as a function of $\vec{k}_\parallel$. The grey scale is defined such that black means low intensity and white high intensity. The data have been taken in a quarter of the surface Brillouin zone, the rest of the image is generated by symmetry. The features A, B, C and D correspond to the surface states in figure 3.

In a free-electron like system a point defect on the surface would be screened by the interference of incoming and scattered Bloch waves. This changes the electron density in the immediate vicinity of the defect and gives rise to long range Friedel oscillations. In our case this is not possible because an incoming electron with wave-vector $\vec{k}_\parallel$ can not be back-scattered into a state with $-\vec{k}_\parallel$, at least not without flipping the spin. These speculations could be checked by scanning tunnelling microscopy (STM) since the Friedel oscillations which are caused by the scattering of the surface state electrons are directly visible [19] and can be related to the surface Fermi line [20, 21]. For a non-spin-degenerate Fermi line, certain Friedel waves should not be observable [22]. As another consequence of lifted spin degeneracy in a two-dimensional system, unusual properties in the superconducting state have been predicted very recently [23].

How relevant are these findings with respect to the superconductivity found in granular systems built from well-defined rhombohedral Bi clusters? The initial model proposed by Weitzel and Micklitz to explain the superconductivity was indeed the presence of a metallic cluster surface which would show ‘surface superconductivity’ and a cluster centre with a low density of states near the Fermi level [5]. Later, however, transport measurements have led to the conclusion that a model which assumes a thin metallic surface and a semimetallic cluster core is probably incorrect [24]. Our measurements now reveal that the Bi(110) surface, which is also present on the clusters [25], is indeed a good metal which could turn into a superconductor at...
sufficiently low temperatures. Moreover, the surface states are found in a narrow gap and their linewidth is relatively large. This is consistent with a long penetration length of the surface state wavefunction into the bulk. This penetration would make a clear distinction of bulk and surface properties impossible for the small clusters. We note, however, that the comparison between a single-crystal surface and the corresponding surface of a very small cluster is problematic in itself. Note that the length of a (110) face on a cluster of a few nm is only of the order of 10 lattice constants and that, moreover, strong structural fluctuations may be present on the smaller clusters.

In summary, we have determined the electronic structure of Bi(110) by high-resolution angle-resolved photoemission. Surface states are found in the projected gap close to the Fermi level in several regions of the surface Brillouin zone. These states show Fermi level crossings and they have effective masses which are much higher than those of most carriers in bulk Bi. The combination of these two facts turns the surface into a better metal than the bulk. While the actual surface structure is unknown, it seems likely that the surface states are related to the dangling bonds which would be expected for the ideal Bi(110) surface. A more metallic surface may, however, not be the only consequence of the reduced dimensionality. We speculate that the large spin–orbit splitting in bulk Bi combined with the loss of inversion symmetry at the surface results in a surface band structure and a surface Fermi line which is not spin-degenerate. This should lead to some peculiar screening properties which should be observable by scanning tunnelling microscopy. For a deeper understanding of the Bi(110) properties, a structural determination is needed. It would also be very interesting to compare our results with first-principles calculations of the geometric and electronic structure.

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