Photoemission study of the Bi(111) surface

F. Patthey and W.-D. Schneider
Institut de Physique Expérimentale, Université de Lausanne, CH-1015 Lausanne, Switzerland

H. Micklitz
II. Physikalisches Institut, Universität zu Köln, Züln, Zülpicher Strasse 77, D-50937 Köln, Germany
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Angle-resolved photoemission spectra of the Bi(111) surface are presented. The results confirm the existence of a surface state in a spin-orbit gap. In addition, a bulk band is found to cross the Fermi energy. These features may be involved in the superconducting properties of granular systems built from Bi clusters. Moreover, the Bi 5*d* core level is found to be shifted at the surface by 0.22 ± 0.02 eV towards lower binding energy, which is in excellent agreement with theoretical prediction.

Granular systems built from well-defined Bi clusters with rhombohedral bulk structure show, in contrast to bulk Bi, the occurrence of superconductivity.[1] The experimental findings of a strong size dependence of T_c could be explained by assuming the occurrence of surface superconductivity due to a strongly increased density of states $N(E_F)$ at the cluster surface. This proposal has been based on earlier observations of a strong increase in $N(E_F)$ for very thin crystalline rhombohedral Bi films.[2] The authors of Ref. 1 suggested that photoelectron spectroscopic studies be performed on bulk Bi surfaces, in order to confirm their proposal of strongly enhanced density of states at the Bi surface.

So far photoemission studies on the semimetal Bi have been scarce. The early investigations were carried out on crystalline, amorphous, and liquid phases of bismuth where the interest was predominantly a comparison between measured[3] and calculated density of states[4] and on the manifestations of the semimetal to metal transition (occurring at the melting point) on the electronic structure.[5–7] Only recently the electronic structure of Bi has attracted renewed interest. Quantum size effects and the temperature dependence of low-energy excitations of thin Bi crystals were investigated by high-resolution electron energy-loss spectroscopy[8] and the electronic structure of the Bi(111) surface was studied by angle resolved photoemission and compared with calculations.[9] A result specifically interesting within the present context is the finding of the existence of a surface state in a spin-orbit gap near E_F.[9] However, since these measurements have been performed at relatively moderate energy resolution (250 meV to 400 meV) we felt that it might be interesting to revisit this compact surface employing a better energy resolution (40 meV). In this way it is hoped to get more detailed insight into the electronic structure of this fascinating semimetal.

The experiments were performed in a custom-built electron spectrometer (VSW) equipped with a high-intensity microwave gas-discharge lamp (GAMMADATA) producing photons of 21.2 eV (He I), 40.8 eV (He II), and 48.4 eV (He II*) energies. The vacuum ultraviolet radiation is monochromatized by a home-built monochromator yielding satellite-free photoelectron spectra.[10] The angular resolution of the spectrometer is $\pm1°$; the energy resolution was chosen to be 40 meV. The Bi(111) sample was a single crystal polished mirrorlike prior to mounting in the vacuum chamber. The sample was subsequently cleaned by cycles of argon sputtering (300 V) and annealing (450 K). Within the detection limit of x-ray and ultraviolet photoemission the surface was found to be free of contaminants. Sharp low energy diffraction spots indicated a well ordered Bi surface with a sixfold symmetry. The photoemission measurements have to be performed at low temperature in order to minimize the phonon-assisted contributions to the spectra since Bi has a low Debye temperature (120 K).[9,11] This was achieved by using a closed cycle He cryostat (20 K) to which the sample was attached. The base pressure in the analysis chamber during the low-temperature measurements was in the low 10^{-10} mbar range.

Figures 1(a) and 1(b) show photoemission spectra obtained at room temperature and at 20 K illustrating clearly the influence of phonon-assisted transitions on the excitation spectra. The spectra have been recorded at normal electron emission. It should be noted that in this geometry states in the (111) direction (from Γ to T) of the three dimensional Brillouin zone are sampled.[4] The difference in the electron wave vector between initial and final state, $|\mathbf{k}_f-\mathbf{k}_i|=\Delta k$, is 2.36 and 3.28 Å^{-1} at 21.2 and 40.8 eV, respectively. The diameter of the volume Brillouin zone in the $\Gamma T\Gamma$ direction in Bi, corresponding to a reciprocal lattice vector $\mathbf{g}$, is 1.547 Å^{-1}.[4] This leads to $k_\perp=\Delta k-ng=0.814$ and 0.1761 Å^{-1} for He I and He II radiation, respectively. Consequently, at 40.8- and 21.2-eV photon energies states near the high-symmetry points Γ and T, respectively, are observed. This fact allows us to compare our results with the ones obtained previously with synchrotron radiation at lower energy resolution.[9] For example, the low-temperature spectra obtained at photon energies around 60 eV and displayed in Figs. 1(b) and 2 of Ref. 9 correspond (apart from photoionization cross section variations) to our low-temperature spectrum shown in Fig. 1(a). The corresponding peaks at 3 and 1.5 eV binding energy (peaks *C*

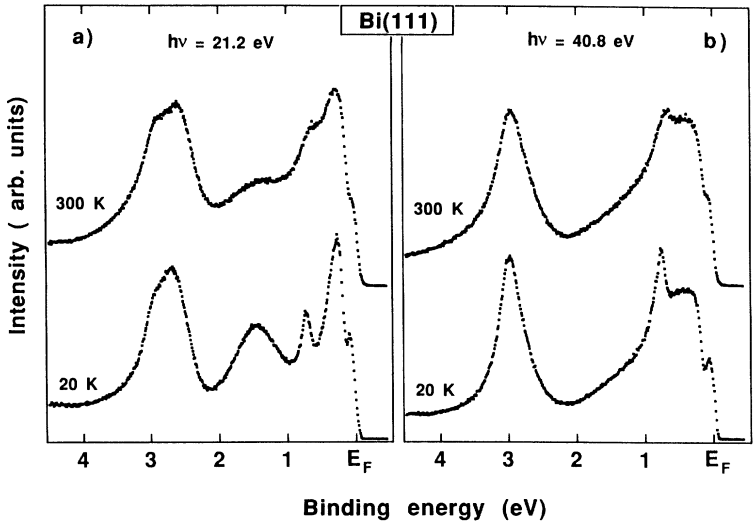

FIG. 1. Photoemission spectra at normal emission from Bi(111) at $T=300$ K and $T=20$ K excited with photon energies of (a) 21.2 eV and (b) 40.8 eV.

and B in Ref. 9) are easily identified whereas near the Fermi energy we distinguish three structures instead of only one (peak A in Ref. 9). Also the spectrum taken at 40.8 eV photon energy and shown in Fig. 1(b) reveals more structure than the corresponding one of Ref. 9 [Fig. 1(b)]. The observation of these details is a consequence of the better energy resolution achieved in the present work.

Since at 21.2 eV photon energy states near the T point of the bulk Brillouin zone are sampled, one of the observed peaks near E_F in Fig. 1(a) should correspond to the surface state reported in Ref. 9. In order to test this assumption the clean sample surface was deliberately contaminated by Ar adsorption at low temperature and, independently, sputtered with Ar ions at room temperature. Both treatments reduce considerably the intensity of the most prominent structures at 3 and at 1.5 eV binding energy. Figure 2 illustrates this phenomenon for the clean and sputtered Bi(111) surface. This experiment clearly confirms the partial surface character of the structure at 3 eV and the existence of the surface state in a spin orbit gap at the (111) surface in Bi as determined in the earlier study.[9] In addition, due to the better energy resolution of the present experiment, two sharp structures near the surface state are recognized in the spectra. Since these structures are also present at 40.8 eV excitation energies we attribute them to bulk transitions from bands (3) and (4) (see Ref. 9) near the Γ point.

The next step in our investigation is to verify the energy dispersion of the surface state. Figure 3 displays off-normal emission spectra of the Bi(111) surface for a photon energy 21.2 eV in the $\bar{\Gamma}\bar{K}$ direction of the surface Brillouin zone.[9,12] The surface state positioned at 0.2 eV binding energy at normal emission ($\theta=0$) disperses as a function of electron emission angle, i.e., as the electron

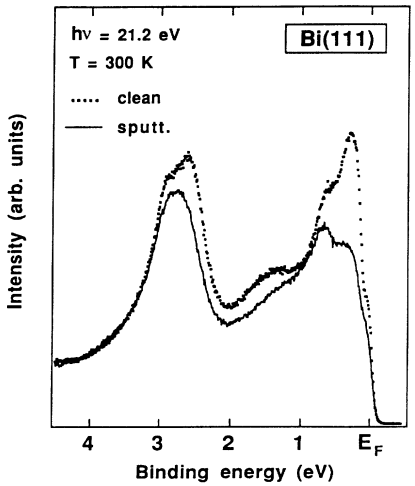

FIG. 2. Influence of surface roughness on the He I (21.2 eV) spectra. The clean Bi(111) surface was sputtered with Ar ions (1 kV, 10 μA) and measured at room temperature.

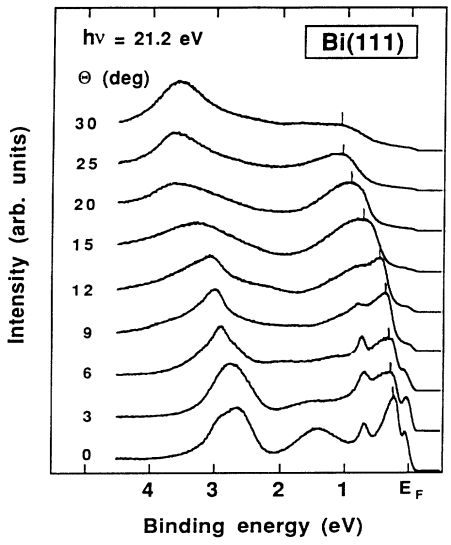

FIG. 3. Off-normal emission spectra of Bi(111) for photon energy of 21.2 eV in the $\bar{\Gamma}\bar{K}$ direction of the surface Brillouin zone.

wave vector $\mathbf{k}_{\parallel}$ is varied. In Fig. 4 we show the energy dispersion of the surface state as obtained from the marked energy positions indicated in Fig. 3. We notice qualitative agreement between the dispersion obtained in this work and the one reported in Ref. 9, which verifies the correct identification of this structure as a surface state. On the other hand, the better energy resolution employed in the present work allows us to follow more precisely the energy dispersion of the surface state. Therefore at the $\bar{K}$ point of the surface Brillouin zone this state is found at 1.2 eV as compared to 1.6 eV in Ref. 9. With a photon energy of 21.2 eV $\mathbf{k}_{\parallel}$ values between the $\bar{K}$ and the $\bar{M}$ points of the surface Brillouin zone cannot be reached so that the resonancelike behavior of this state reported previously using tunable synchrotron radiation[9] is not observable.

From earlier calculations[4,9] it is known that the density of states (DOS) in the ΓT direction of the bulk Brillouin zone is derived mainly from p states. The same holds true for the surface DOS at the $\bar{\Gamma}$ point.[9] It is difficult to imagine how a surface state bound by 0.2 eV (minimum) can have any impact on the superconductivity, since the Debye energy is 4 meV (Ref. 13) and the superconducting energy gap is even smaller. On the other hand, the calculated surface DOS displayed in Fig. 3 of Ref. 9 shows a finite contribution from $p_{y,y}$ orbitals at E_F. Our $\mathbf{k}$ resolved energy distribution curves shown in Fig. 1, sampling the ΓT direction, clearly display a sharp Fermi edge indicating a finite density of states at E_F. A finite DOS has also been observed in x-ray photoemission spectra from liquid (metallic) Bi where a value of $N(E_F)=0.4\pm0.2$ states per eV per atom, typical for a good metal, has been derived.[6] Comparing this photoemission result with estimations from new transport measurements on Bi clusters [0.56 states per eV per atom, obtained from the magnetic field dependence of the superconducting transition temperature in granular films built from Bi clusters with average diameter of 4.2 nm (Ref. 14)], reasonable agreement is obtained. Thus the density of states for metallic Bi and for the Bi clusters are of comparable magnitude. The question how the specific electronic structure of the Bi(111) surface is involved in the formation of the superconducting state of Bi clusters, however, must await the answers of further experiments.

Finally, in the context of surface phenomena we have measured a surface core-level shift (SCS) for the Bi $5d_{5/2}$ level using 48.4-eV photon energy and an electron takeoff angle of 45° in order to enhance the surface sensitivity of the measurement. Our results are summarized in Fig. 5. As already mentioned for the valence-band spectra, the reduced phonon broadening at low temperature permits us to observe structure in the line shape. By decreasing the electron takeoff angle an intensity reduction (increase) in the shoulder at higher (lower) binding-energy is observed in Fig. 5. The same behavior is noticed on sputtered rough surfaces. Whereas the first observation can also be due to photoelectron diffraction the second one clearly indicates that the lower binding-energy structure is associated with emission from a surface shifted Bi $5d_{5/2}$ core level. The value of the SCS, obtained by fitting the data with two Lorentzians (shown in Fig. 5) convoluted with Gaussians (representing the experimental resolution)[15] is found to be 0.22 ± 0.02 eV. The direc-

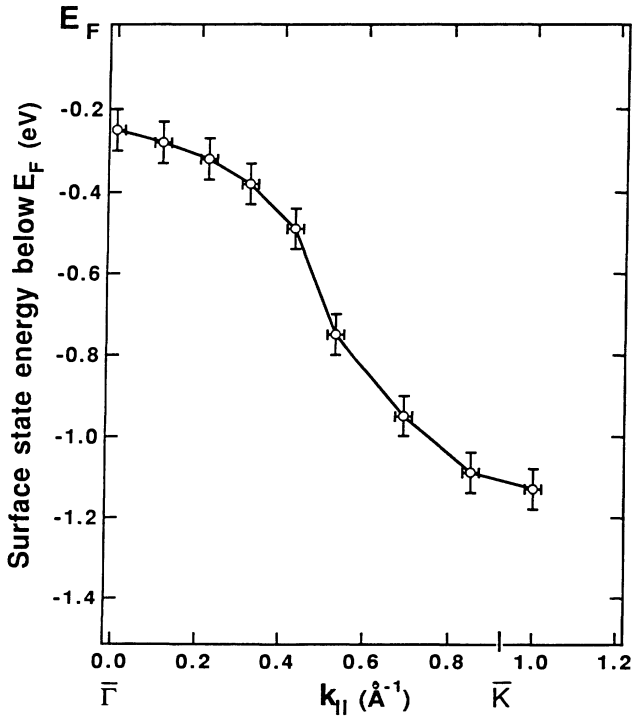

FIG. 4. Dispersion of the surface state energy along the $\bar{\Gamma}\bar{K}$ direction. The curve connecting the experimental points is drawn to guide the eyes.

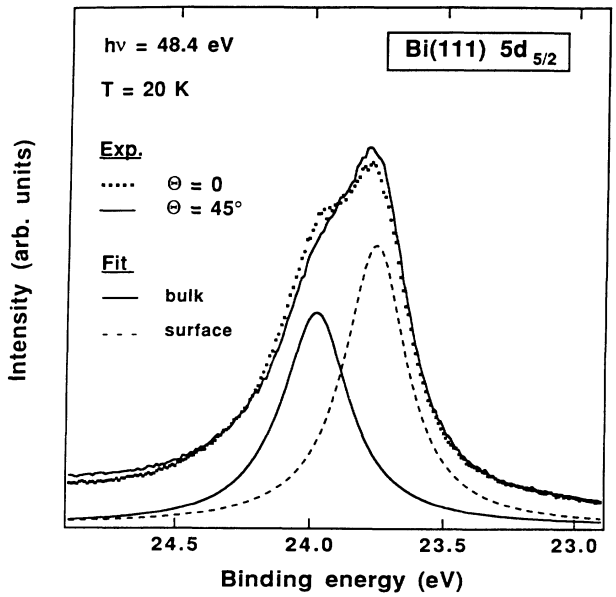

FIG. 5. Bi $5d_{5/2}$ core-level spectrum excited with 48.4 eV photon energy at a sample temperature of 20 K. The two Lorentzians resulting from the line-shape analysis (see text) indicate the bulk (full curve) and surface components (dashed curve).

tion and magnitude of this shift is in excellent agreement with a theoretical prediction based on a thermochemical model.[16]

To summarize, these measurements confirm the existence of a surface state in a spin-orbit gap at the Bi(111) surface near E_F. Moreover, a bulk derived band is found to cross the Fermi level contributing to an enhanced density of states at this surface and which might be involved in the formation of the superconducting state found recently in Bi clusters. For the Bi atoms in the surface layer a surface core-level shift of the Bi 5*d* level of 0.22 eV is observed which is in agreement with theoretical predictions.

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