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Electronic structure of the Bi(111) surface

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Both measured angle-resolved photoemission spectra and the calculated electronic structure of the (111) surface of Bi are presented. We find good agreement between theory and experiments. The results show the existence of surface states in spin-orbit gaps.

Intrinsic electronic surface states appear always at energies inside the bulk band gaps. Surface states in energy gaps caused by the periodicity of the crystal potential have been widely studied both experimentally and theoretically during the last fifteen years, both in semiconductors and in metals.[1] However, not much work has been aimed at the study and characterization of surface states in spin-orbit gaps.[2-7]

The purpose of this work is to study from both the experimental and theoretical points of view the electronic structure of the semimetal Bi(111) surface in order to investigate the existence of surface states in spin-orbit gaps. The reason for choosing Bi in our study is threefold: First, its spin-orbit coupling is large. Second, the (111) surface does not reconstruct, and the analysis is thereby simplified. Third, since the $5d$ bands are occupied, many-body problems in narrow partially filled bands are avoided.

The experiments were performed at the Laboratoire pour L'Utilisation du Rayonnement Electromagnétique at Orsay. The monochromatized storage-ring light from either a toroidal-grating monochromator or else a normal-incidence monochromator served as light source. The measurements were performed with the light beam set at an angle of incidence. The resolved electron distribution curves were recorded using a spherical photoelectron spectrometer with an angular resolution of $\pm 0.7°$. The spectra were obtained for photon energies between 7 and 100 eV with an overall energy resolution smaller than 250 meV for photon energies below 40 eV and ranging from 250 to 400 meV when the photon energy was increased from 40 to 100 eV.

The Bi(111) samples were single crystals cleaved at low temperature in order to obtain mirrorlike surfaces either *in situ* or in air prior to mounting in the vacuum chamber. In the latter case the samples were subsequently cleaned by cycles of argon sputtering (300 V) and annealing (150 °C). The cleanliness of the surface was checked by Auger spectroscopy and its crystalline order by low-energy electron diffraction (LEED). A very intense diffraction pattern with sixfold symmetry was observed in LEED. The results discussed in this work were mainly obtained using this second sample-preparation procedure.

Measurements have to be performed at low temperature in order to minimize the phonon-assisted contributions to the photoemission spectra since Bi has a low Debye temperature (120 K).[8] The low-temperature results require the use of a variable-temperature He-flow cryostat (200–450 K) specially designed for photoemission experiments. The base pressure in the chamber during the low-temperature measurements was around 10^{-10} mbar.

Figure 1 gives an overview of the more representative results obtained at normal incidence for photon energies between 40 and 66 eV. Figures 1(a) and 1(b) show the results obtained at high (300 K) and low (20 K) temperatures, respectively. It should be noticed that by varying the photon energy at normal emission we sample the states in the (111) direction (from Γ to T) of the three-dimensional Brillouin zone.[9]

In the curves of Fig. 1 we distinguish five different peaks (labeled A–E), corresponding to emission from the s bands [peaks D (D') and E] and the p bands (peaks A, B, and C), well separated by an energy gap of the order of 3 eV. We first observe that only peaks B, D (D'), and E exhibit significant dispersion with photon energy and therefore can be identified as structures due to emission from the three-dimensional bulk bands. The dispersion of the s- (p-) like bulk bands can then be obtained using standard band-mapping methods [high-symmetry points Γ and T are easily located at the final-state energies (40.5 eV)/E_F and (88 eV)/E_F].

Peak C does not show any dispersion over the major part of the photon energy range between 40–110 eV except near 57 eV (the final state being in the vicinity of the T point). However, a comparison between the spectra obtained from samples cleaved in vacuum and from sputtered samples reveals that this structure, at these energies, can be identified as being due to indirect transitions produced by the surface roughness. The emission intensity of this peak shows also the periodic oscillatory behavior with respect to the final-state wave vector characteristic of surface states studied by Louie *et al.* on the surface states of the Cu(111) surface.[10]

Peak A is clearly observed for photon energies between 47.5 and 67.5 eV (near the T point for the final state), in the low-temperature data. This variation of the intensity, much stronger than the corresponding one for bulk structures, is due to the fact that the surface has a lower Debye temperature than the bulk.[11,12] This structure is also very sensitive to surface contamination as is shown in Fig. 2,

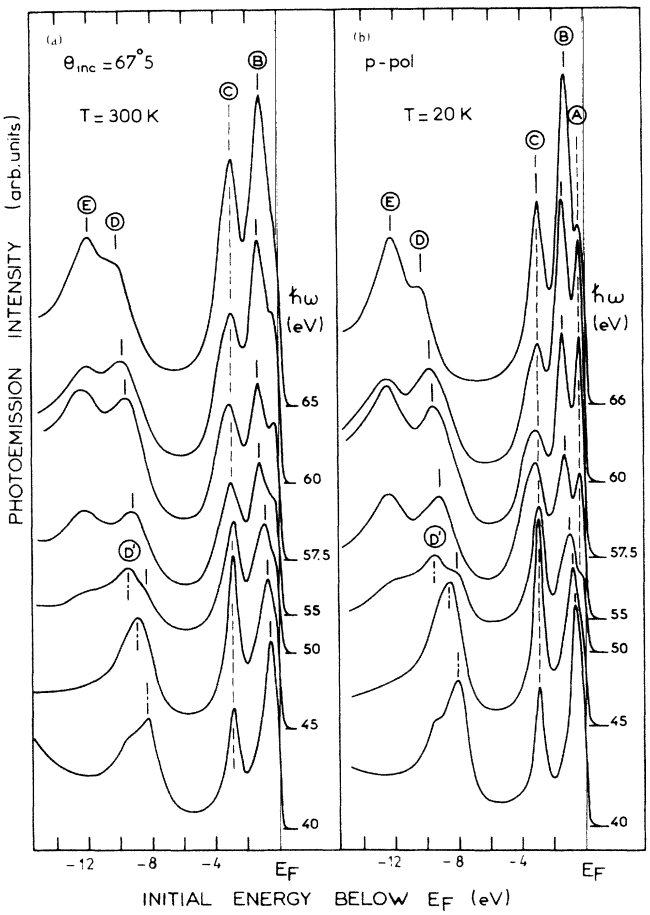

FIG. 1. (a) Normal photoemission spectra of Bi(111) at $T=300$ K and (b) $T=20$ K for various photon energies between 40 and 65 eV. Notice the strong temperature dependence of peak labeled A at energies around 57.5 eV.

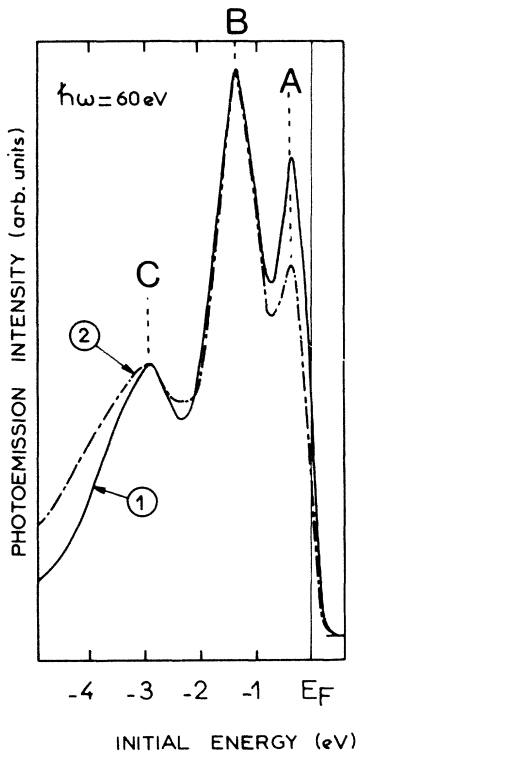

FIG. 2. Influence of contamination on the spectrum near the Fermi level ($T \approx 77°$). Curve 1 was obtained before contamination and curve 2 after exposure to 2 L of residual gas (mainly O_2 and H_2).

where the normal emission is plotted against binding energy or a photon energy of 60 eV, just after the cleaning process (curve 1) and after 2 L (1 L $=10^{-6}$ torr sec) exposure to residual gas (mainly O_2 and H_2O). This surface character is stressed by the fact that since the holes in bismuth are near the T point in the Brillouin zone[13] any structure close to E_F in the vicinity of this point has to have surface character.

The above information allows us to conclude that peaks A and C have surface character although the latter, which shows less emission-intensity variation with temperature and less sensitivity to contamination than the former, might have an important bulk contribution. We will therefore concentrate in the rest of this work on the characterization of the states corresponding to the peak labeled A since it is in an energy region where the spin-orbit interaction has very important effects on the bulk band structure. To this end we have calculated the electronic structure of bismuth and we have also calculated its (111) surface electronic distribution. The model tight-binding Hamiltonian used includes three p orbitals per site (hybridization with the s orbitals is small since the s-like and the p-like bands are well separated in energy).[14] The p orbitals interact when located on nearest- and next-nearest-neighbor atoms. Also the deviation from the cubic structure of the bismuth $A7$ structure is reflected in the atomic energies of the p orbitals. The model Hamiltonian also includes a spin-orbit term of the form

$$H_{S\text{-}O}=\xi \mathbf{L}\cdot\boldsymbol{\sigma} \ .$$

This term has been added to the Hamiltonian in the manner indicated in Ref. 15. The bulk band structure is

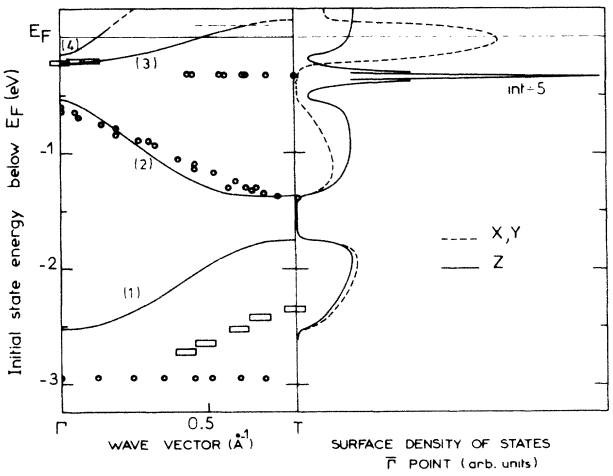

FIG. 3. Experimental and calculated energy band along the ΓT direction. The calculated surface density of states at the Γ point is also presented. The open circles and rectangles represent the experimental points obtained at high ($\hbar\omega > 40$ eV) and low ($\hbar\omega < 20$ eV) photon energy. The theoretical results (shifted 0.2 eV downwards) are presented by a continuous line.

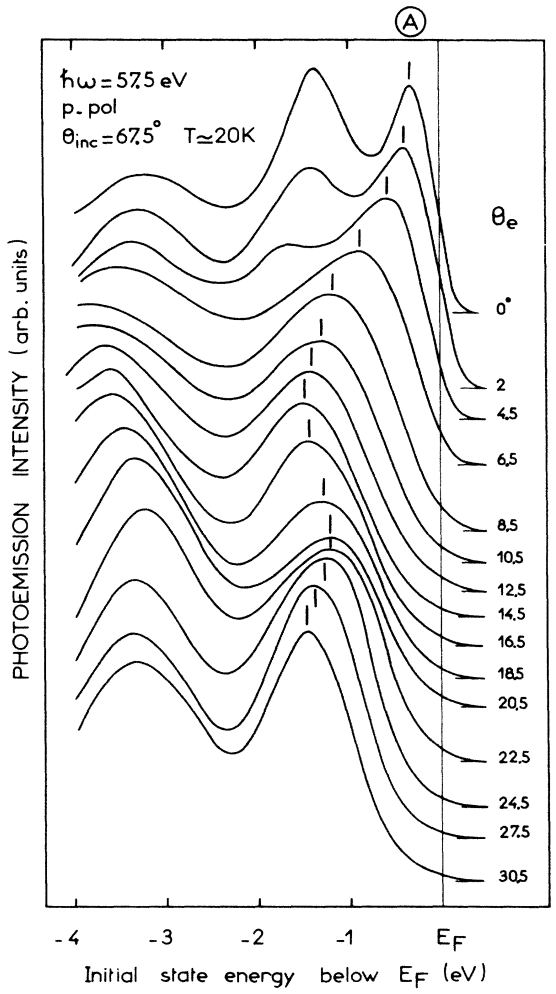

FIG. 4. Off-normal emission spectra of Bi(111) for photon energy 57.5 eV in the $\bar{\Gamma}\,\bar{K}\,\bar{X}$ direction of the surface Brillouin zone. The position of the $5d_{5/2}$ level position is $(-23.9\text{ eV})/E_F$ (see Ref. 14).

calculated in the usual way and to calculate the surface electronic structure we use the Green's-function transfer matrix method.[16] Results of the calculation as well as the experimental $E(k_\perp)$ points obtained assuming a free-electron dispersion for the final states are shown in Fig. 3. There is a reasonable agreement between the theory and the experimental bulk bands although the lower p band is not as well reproduced in the calculation as in the previous calculation of Golin[17] and Ferreira[18] using the pseudopotential and the augmented-phase-wave methods, respectively. The theoretical bands have been shifted downwards 0.2 eV for a better presentation.

We immediately notice in Fig. 3 the existence of a well-

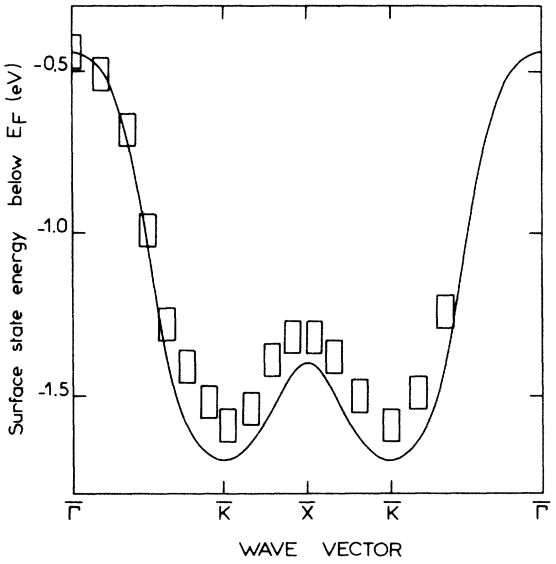

FIG. 5. Dispersion of the surface state energy along the $\bar{\Gamma}\,\bar{K}\,\bar{X}$ direction. The experimental points are represented by rectangles and the theoretical results are represented by a continuous line.

characterized bona fide surface state within the spin-orbit gap. Although the existence of this surface state is mainly due to the abrupt termination of the crystal potential due to the surface, its particular energy position is governed by the spin-orbit gap. The states associated with the surface state have mostly p character as the analysis of the p-like partial densities of states reveals (see Fig. 3). The resonancelike flat band at -3.0 eV is not reproduced in our calculations. This is probably due to the incorrect description of the lower p band in the model.

In order to complete the study of the surface states we have also measured and calculated their energy dispersion parallel to the surface. Results for the ion-bombarded surface are shown in Fig. 4, where the surface symmetry of the band is evident and the position in energy of the surface state is easy to follow. In Fig. 5 we show the calculated energy dispersion of the surface state discussed above (which far from the $\bar{\Gamma}$ point becomes a resonance) along with the experimental results. We notice a good agreement between theory and experiments which verifies the correct characterization of the surface state.

In this work we have been able to observe and characterize a bona fide surface state in the spin-orbit gap of the (111) surface of bismuth. In spite of the experimental difficulties of dealing with a low-Debye-temperature material like Bi the regularity and flatness of its surface make it an excellent candidate to study the effect of a large spin-orbit coupling on the surface electronic structure.

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