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Intrinsic Surface State on Be(0001)

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Abstract

Using monochromatized synchrotron radiation in the range 24-30 eV, we have recorded angle-resolved photoemission spectra from a clean Be(0001) crystal face. A surface state located in a band gap around $\bar{\Gamma}$ with an initial state energy of -2.8 eV in normal emission was found. For $\vec{k}_{//}$ along the $\bar{\Gamma}\bar{M}$ line the surface state disperses upwards and passes E_F at about 55 % of the distance to the SBZ boundary.

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INTRODUCTION

Among simple metals beryllium shows the largest deviation from a free-electron-like band structure. For metallic Be the bonds between the closely packed Be atoms are partly covalent (1,2) and large energy bandgaps are found in the band structure (3). The largest of these bandgaps is centered around the Γ point in the reciprocal space and in energy located at the Fermi level (E_F). It causes the total density of states at E_F to be very low for Be. In a chemist view this is the bonding-antibonding gap for the covalent sp-orbitals of Be. A number of theoretical band structure calculations have shown that the hybridization between s and p wave functions is strong. They also show that exchange and correlation effects are important to include to obtain an accurate calculation of the electron bands (1,2,4). In spite of the theoretical efforts, the experimental information on the electronic structure of Be is limited. The experimental results reported mainly treat the Fermi level properties of the Be electron bands (5).

Other simple metals like Mg, Al, and Zn with an electron band structure "similar" to Be have been successfully investigated using angle-resolved photoemission spectroscopy (ARPES), (6-9). Here both transitions between bulk electron bands and excitations of electrons located in surface state bands have been detected and a knowledge of the bulk and surface electron structure away from E_F is obtained. The surface states detected are located in the energy band gaps obtained by projecting the 3-dimensional band structure onto the 2-dimensional surface Brillouin zone (SBZ), i.e. bandgaps in the $E(\vec{k}_{//})$ band structure. This type of bandgap is also found for different single crystal faces of Be. We have performed an ARPES study of the Be(0001) crystal face to detect surface states located in the $E(\vec{k}_{//})$ bandgaps and if possible to map the bulk electronic structure from direct transitions observed. The photon energy was varied in the range 24-30 eV and the azimuthal angle was set to probe electron states in the symmetry plane $\bar{\Gamma}\bar{A}\bar{L}\bar{M}$ or in terms of the SBZ along the symmetry line $\bar{\Gamma}\bar{M}$ (Fig. 1). The light was polarized in the horizontal plane and by using

an angle of incidence of 45^0 we had the possibility to detect electronic states of different symmetries.

EXPERIMENTS

The experiments were performed at the Hamburger Synchrotron Strahlungslabor, HASYLAB. The monochromatized synchrotron light output from an 1m Seya-Namioka monochromator served as a light source. The angle resolved electron distribution curves (AREDC's) were recorded using an ADES 400 photoelectron spectrometer with an angular resolution of $\pm 2^0$ (10). The slits of the 1m Seya-Namioka monochromator and the pass energy of the electron energy analyzer were set to obtain a total energy resolution of $\leq$0.3 eV in the spectra reported.

The sample was a Be(0001) single crystal that had been spark cut, mechanically polished and finally electro-polished (5% perchloric acid and 95% ethyl alchohol) to obtain a mirror-like surface.

The crystal was cleaned in situ by repeated cycles of argon sputtering and annealing (600^0C, 30 min), the base pressure at the start of the cleaning procedure was 7×10^{-11} Torr (9×10^{-9} Pa). The cleaning procedure produced an intense six-fold symmetric diffraction pattern as observed in LEED. The diffraction pattern was used to choose the proper azimutual orientation of the sample, i.e. $\bar{\Gamma}\bar{M}$ line in the horizontal plane.

RESULTS AND DISCUSSION

AREDC's for electrons emitted in the normal direction ($\theta_e=0^0$) from a Be(0001) surface are shown in Fig. 2. The fairly structureless spectra are dominated by a peak at an initial-state energy of -2.8 eV, the peak is located at this initial-state energy for all photon energies used in the energy interval 24-30 eV. We also observe an increasing intensity of the -2.8 eV peak with increasing photon energy in the same energy interval. Apart from the -2.8 eV peak, the only observable structure is the Fermi edge. The recorded intensity at the Fermi edge in normal emission

is low compared to the Fermi edge intensity recorded in normal emission from the Mg (0001) surface if they are normalized to corresponding background emission (6).

The polar-angle dependence of the photoemission was studied in the ΓALM plane, $\bar{\Gamma}\bar{M}$ line in the SBZ. Figure 3 displays AREDC's for different polar angles of emission (θ_e). As shown in Fig. 3 the -2.8 eV peak disperses upwards in energy when θ_e is increased and crosses E_F at about $\theta_e = 23^0$. We observe in Fig. 3 that the -2.8 eV peak becomes sharper when its initial-state energy decreases.

On the right-hand side of Fig. 4 we plot the position in initial-state energy (E_i) as a function of momentum parallel to the surface ($\vec{k}_{//} = (\hbar\omega + E_i - \phi)\frac{2m}{\hbar^2})^{\frac{1}{2}} \sin\theta_e$), also shown in the right-hand side of Fig. 4 is the calculated bulk electron energy bands along ΓM. The two upper bands in the figure represent the highest (in initial-state energy) occupied bulk electron bands in the ΓALM plane (1). The left-hand side of Fig. 4 shows the calculated bulk electron energy bands along ΓA (1). Above 10 eV we have taken the final-state bands to be free electron-like parabolas adjusted to fit the calculated bands at the lowest unoccupied A_1 point and with an effective mass (m_e) of 1 (11). As seen in Fig. 4, a large band gap opens up between the two lowest lying Δ_2 bands. Along the $\bar{\Gamma}\bar{M}$ line in the SBZ the lower edge of this band gap is given by the energy bands along ΓM in the bulk BZ. The bandgap shrinks with increasing $\vec{k}_{//}$ and its center of gravity moves upwards. In Fig. 4 we have plotted the dispersion ($E_i(\vec{k}_{//})$) of the -2.8 eV peak for $\vec{k}_{//}$ values along the ΓM line, we observe that its energy position falls within the bandgap and its dispersion is almost parallel to the lower band edge.

From our experimental data we deduce that the -2.8 eV peak falls within a bandgap of the 2-dimensional projected band structure of the Be bulk bands

onto the (0001) crystal face. Its initial-state energy position stays constant for different photon energies when we observe the -2.8 eV peak in normal emission. These two observations are consistent with assigning the -2.8 eV peak to emission from a surface state band, the surface state band being located in the band gap opened up between the first two bands of Δ_2 symmetry along the ΓA line.

The surface state wave function at a specific $\vec{k}_{//}$ value can be constructed by adding bulk wave functions of the same $\vec{k}_{//}$ but allowing for all possible values of momentum perpendicular to the surface ($\vec{k}_\perp$) to contribute to the expansion. It has also been noted that the dominating $\vec{k}_\perp$ components in this expansion come from regions in $\vec{k}$-space where the surface state band and one of the enclosing bulk bands are close in energy (12). The existence of all possible $\vec{k}_\perp$ in the surface state wave function explains the stability in initial-state energy for different photon energies, we will always have a possible transition for any $\vec{k}_\perp$ at the initial-state energy of the surface state at a given $\vec{k}_{//}$-value ($\vec{k}_{//} = 0$ in this case). Using this scheme we also have a possible explanation to the increasing intensity of the surface state in the normal direction for increasing photon energies. The surface state at $\vec{k}_{//} = 0$ will be a super position of bulk wave functions with symmetries Δ_1 and Δ_2, $\vec{k}_\perp$ values in the interval ΓA . We have to include both Δ_1 and Δ_2 bulk symmetries since the surface state will have the Λ_1 symmetry which is compatible with both Δ_1 and Δ_2 (13). The surface state will be mainly composed of bulk wave functions with $\vec{k}_\perp$ values close to the second Γ point (Γ_3^+) but will have finite contributions from other $\vec{k}_\perp$ values. We then expect a major maxima in the surface state intensity when the photon energy connects the second point to a final state band of Δ_2 symmetry ($\hbar\omega \sim 90$ eV), but there could also be a possibility of a maxima when the photon energy takes the surface state initial energy to a critical point in a Δ_1 final state band ($\hbar\omega \sim$ 30 eV). In other words we state that the symmetry of the surface state is compatible with both Δ_1 and Δ_2 symmetry wave functions and transitions to both Δ_1 and Δ_2 symmetry final state bands are possible. An experimental proof of the Λ_1 symmetry was obtained by decreasing the angle of light incidence (θ_i). At small θ_i the intensity of the -2.8 eV peak reduced drastically. Finally we found the -2.8 eV peak to disappear upon contamination, our sample had to be recleaned every second hour.

In the polar-angle spectra (Fig. 3) we observe that the -2.8 eV peak sharpens and gets an increasing visibility for higher angles of θ_e. We interpret this as due to an increased life time when its initial-state energy comes closer to E_F, where we expect the Auger decay rate to be low, especially for Be with its low density of states in this energy region.

We observe no direct transitions in normal emission. This is obvious as direct transitions into primary cones are symmetry forbidden in normal emission for photon energies used in this experiment. For bulk bands the surface cannot relax the symmetry of the wave functions and cause cross transitions Δ_1 to Δ_2 (12). The low Fermi edge intensity observed is also explained by the electronic structure of Be along the ΓA line, there is no state available at E_F for normal emission and all observed electrons at E_F have to be from an indirect excitation process or final state scattered.

SUMMARY

Using photon energies 24-30 eV, we have observed a prominent structure in normal emission spectra, located at -2.8 eV initial-state energy. The peak falls in a bandgap of the projected 2-dimensional bandstructure of the bulk bands onto the Be (0001) surface. Its dispersion as a function of $\vec{k}_{//}$ parallels the lower band edge along the ΓM line and crosses the Fermi level halfway to the BZ boundary. We interpret this peak to be due to a surface state located in the bandgap at the second Γ point opened up by the crossing of two Δ_2 bands, the surface state will have Λ_1 symmetry.

The experiment confirms the expectation of a large bandgap centered at and responsible for the low density of states predicted for Be at E_F.

No direct transitions between Be bulk bands were detected mainly due to the limited photon energy range available.

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FIGURE CAPTIONS

Fig. 1 Bulk Brillouin zone (below) and surface Brillouin zone for a hcp lattice.

Fig. 2 Experimental AREDC's for photoelectrons emitted normal to the Be (0001) crystal face for photon energies between 25-30 eV.

Fig. 3 Experimental AREDC's for Be (0001) at different polar angles. The polar angle is varied in the ΓALM plane with $\hbar\omega$= 24 eV.

Fig. 4 Energy bands for Be in the Γ A (left) and Γ M (right) directions. Bands below 10 eV are from calculations of Inoue and Yamashita (Ref. 1). The dots in the right-hand side of the figure show the experimental surface state dispersion.

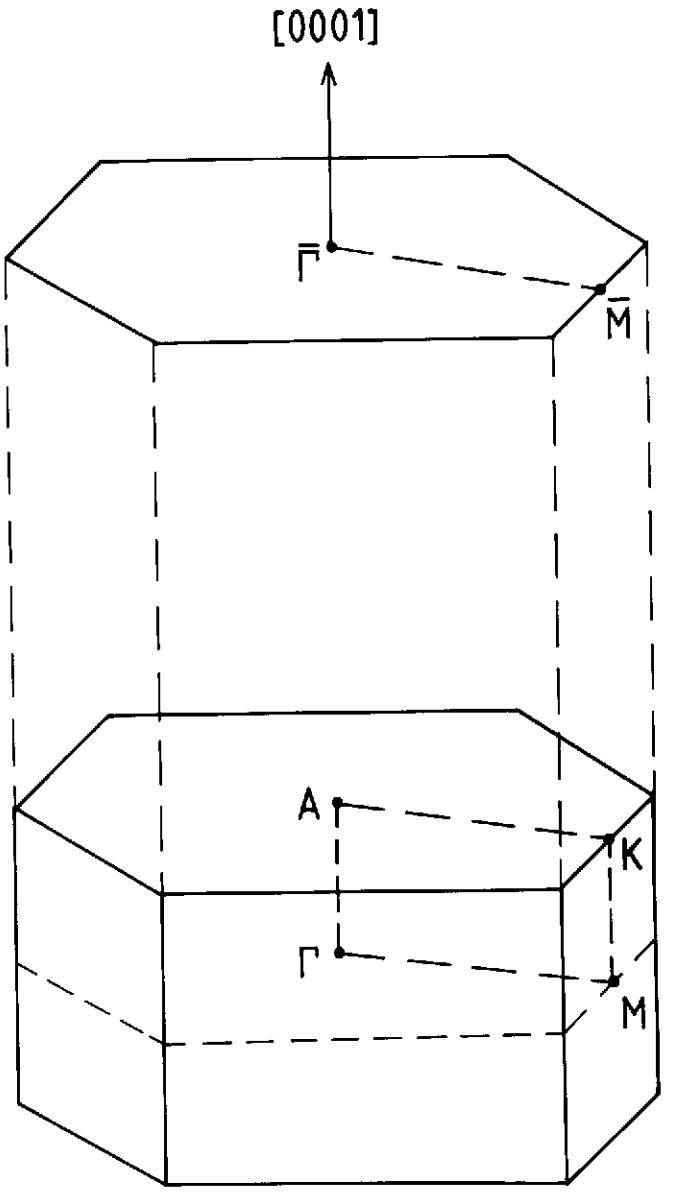


Fig.1

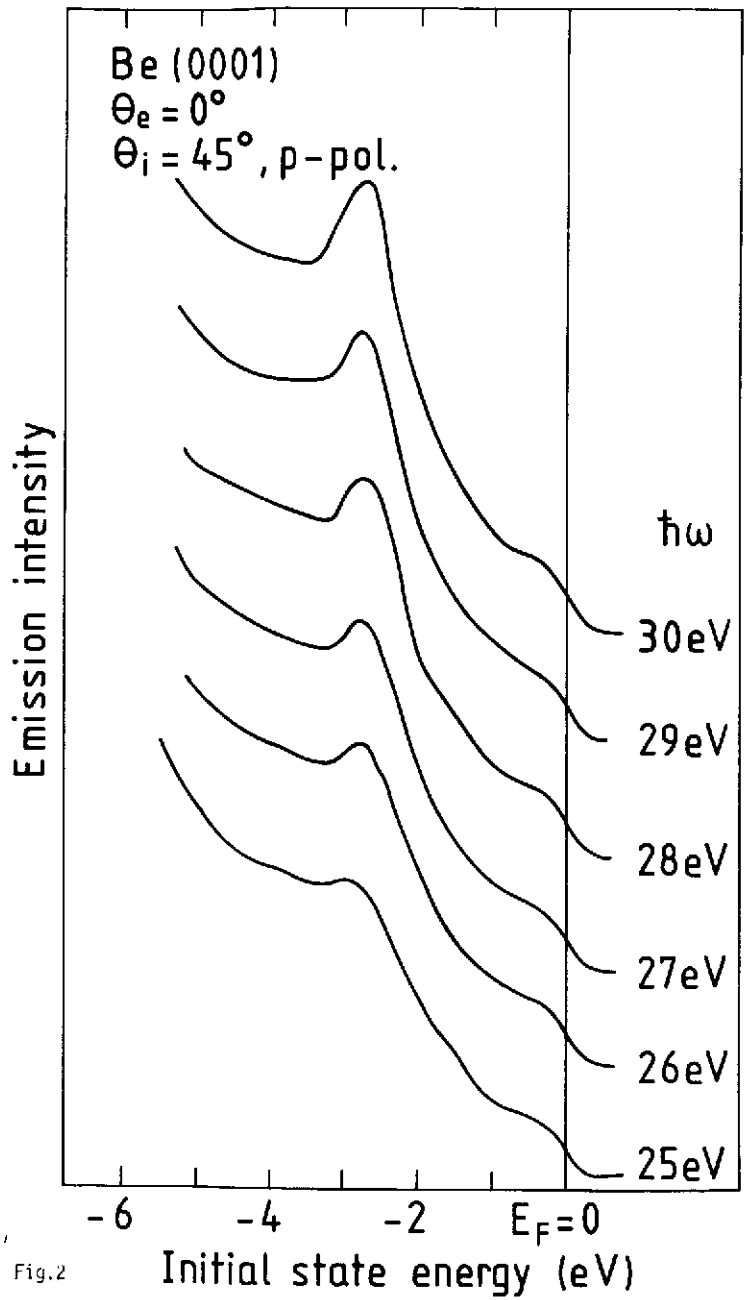

Be (0001)
$\theta_e = 0°$
$\theta_i = 45°$, p-pol.
$\hbar\omega$
30eV
29eV
28eV
27eV
26eV
25eV
Emission intensity
-6
-4
-2
$E_F = 0$
Initial state energy (eV)

Fig.2

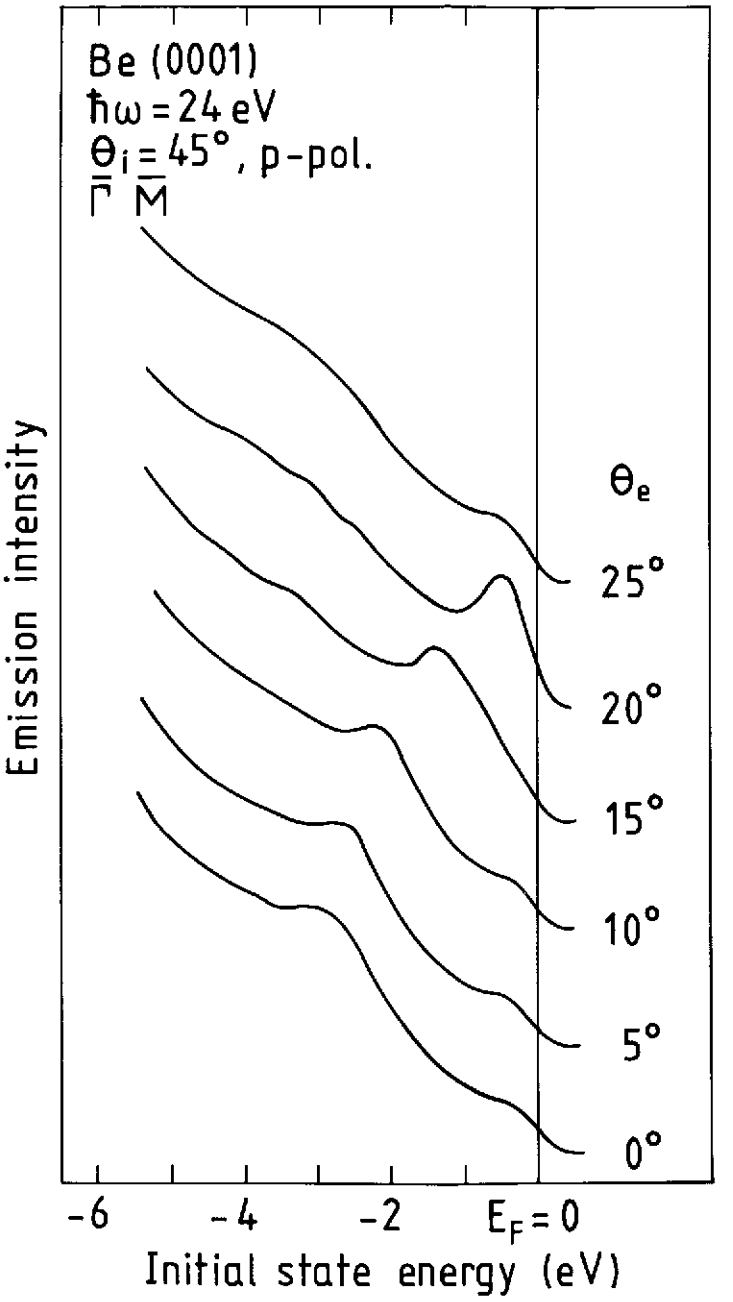
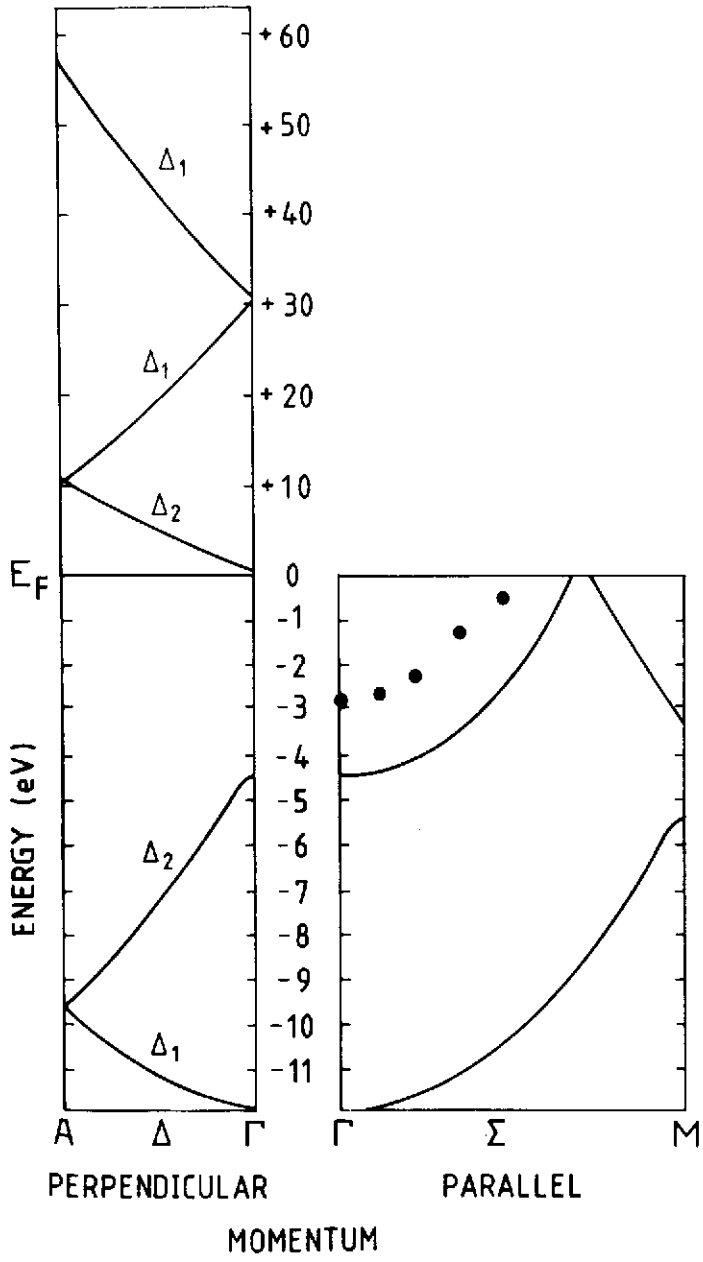

Be (0001)
$\hbar\omega = 24$ eV
$\theta_i = 45°$, p-pol.
$\bar{\Gamma}$ $\bar{M}$
θ_e
25°
20°
15°
10°
5°
0°
Emission intensity
-6
-4
-2
$E_F = 0$
Initial state energy (eV)

Fig.3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+50
+40
+30
+20
+10
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
E_F
ENERGY (eV)
Δ_1
Δ_1
Δ_2
Δ_2
Δ_1
A
Δ
Γ
Γ
Σ
M
PERPENDICULAR
PARALLEL
MOMENTUM

Fig.4