

Circular dichroism in photoemission as a fingerprint of surface band structure: The case of ZnSe(001)- $c(2 \times 2)$

F. Vidal,¹ M. Marangolo,¹ P. Torelli,² M. Eddrief,¹ M. Mulazzi,³ and G. Panaccione³

¹*Institut des Nanosciences de Paris, UMR 7588 CNRS-Universités Pierre et Marie Curie-Paris 6 et Denis Diderot-Paris 7, Campus Boucicaut, 140, rue de Lourmel, 75015 Paris, France*

²*INFN-CNR, National Research Centre for nanoStructures and bioSystems at Surfaces (S3), Via Campi 213/A, 41100 Modena, Italy*

³*TASC Laboratory INFN-CNR, in Area Science Park, S.S.14, Km 163.5, I-34012 Trieste, Italy*

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Measurements of circular dichroism in the angular dependence (CDAD) of photoemission from core levels and valence bands of the ZnSe(001)- $c(2 \times 2)$ surface are presented. Due to the lowering of the surface symmetry compared to the bulk, the CDAD of surface-related spectral components and of bulk components exhibit different polar variations. We propose a way to identify experimentally surface-related bands in the valence-band photoemission spectra based on these symmetry considerations.

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Angle-resolved photoemission spectroscopy is a powerful method to study surface electronic band structure. However, the separation of bulk- and surface-related spectral features in photoemission spectra is difficult in general. It often calls for careful comparison between state-of-the-art surface band structure calculation and experiments.

X-ray photoemission spectroscopy (XPS) and x-ray photoemission diffraction (XPD) experiments are usually carried out using linearly polarized light. Using circularly polarized light, it is possible to record the circular dichroism in the angle dependence (CDAD) of photoelectrons. CDAD is a spectroscopic technique that is sensitive to the symmetry of the experiment.¹⁻³ Its existence has been predicted by Dubs *et al.* for oriented molecules⁴ and was confirmed experimentally by Westphal *et al.*⁵ It has been used to study single-crystal surfaces,^{6,7} adsorbed atoms^{8,9} and oriented adsorbed molecules at surfaces,^{10,11} and more recently chiral metal surfaces¹² and adsorbed chiral molecules.^{13,14}

For a given detection angle of the photoelectrons, the photoemission intensity will depend on the helicity (σ^+ for right circular polarization and σ^- for left circular polarization) of the incoming photons. Such an effect is purely dipolar¹⁵ and results from interference caused by helicity-related phase differences of the photoelectron wave functions.² It arises even for nonmagnetic systems and does not require spin-orbit coupling. CDAD can be used in principle to study chiral centers at surfaces.^{13,14} This handedness-related sensitivity could be used to detect mirror planes of a sample and, in principle, to compare surface and bulk symmetry. This suggests a possibility to disentangle surface states from bulk states using CDAD, provided that surface and bulk components are spectrally resolved.

For this reason, we choose as a model system the reconstructed ZnSe(001)- $c(2 \times 2)$ surface. This system offers the advantage that surface and bulk components of the Zn 3d photoemission peak are well separated, enabling a clear spectral distinction between signals coming from Zn surface atoms and from bulk. The aim of this study is to check whether CDAD can bring some new information, such as criteria to identify surface and bulk related spectral features. The reconstructed ZnSe(001)- $c(2 \times 2)$ surface has been stud-

ied recently using surface x-ray diffraction combined with density functional theory calculation.¹⁶ It was shown that the equilibrium $c(2 \times 2)$ -surface structure can be described by a Zn-vacancy model consisting of half a monolayer of Zn atoms on the (001) surface of a Se-terminated ZnSe bulk crystal and vertical as well as lateral relaxations.

High-quality ZnSe epilayers were prepared in a molecular beam epitaxy (MBE) multichamber facility equipped with interconnected III-V and II-VI growth chambers, in which 10-nm-thick undoped pseudomorphic ZnSe epilayers were grown on a GaAs buffer layer deposited on highly *n*-doped GaAs(001) substrate.^{17,18} At the end, the ZnSe epilayers were capped with an amorphous Se layer, a technique that has proved to be very efficient in preventing contamination during sample transportation.¹⁹ Once in the photoemission setup, samples were slowly heated up to 350 °C under ultra-high vacuum in order to remove the Se capping layer and stabilize the $c(2 \times 2)$ -Zn-terminated surface. After this procedure, the surface was further controlled by low-energy electron diffraction (LEED). LEED was also employed in order to perform a careful alignment of the sample with respect to the incoming beam and detector axis.

Photoemission experiments were performed on the APE-INFN surface laboratory and beamlines at the ELETTRA storage ring of Sincrotrone Trieste. Core levels and valence-band emission were measured with a high-resolution spectrometer (Scienta 2002). The experimental arrangement is sketched in Fig. 1(a). The circular polarized photons impinge the sample surface with an incident angle of $(\vec{q}, \vec{n}) = 45^\circ$. The experiments were performed with a photon energy of 45.5 eV. At this energy, the kinetic energy of the photoelectrons is ~ 30 eV for the Zn 3d and ~ 37 eV for the valence band, resulting in a mean free path of ~ 4.5 and ~ 4.3 Å, respectively.²⁰ This choice enabled a nearly optimal surface sensitivity for the whole spectral range investigated. The photoelectrons were detected in the perpendicular plane as a function of the polar angle θ within an angular range of $\pm 7^\circ$ about the nominal angle. By changing the latter it is possible to span a wide angular range $[-15^\circ, +15^\circ]$ in the present case.

Zn 3d and valence-band spectra were recorded for azi-

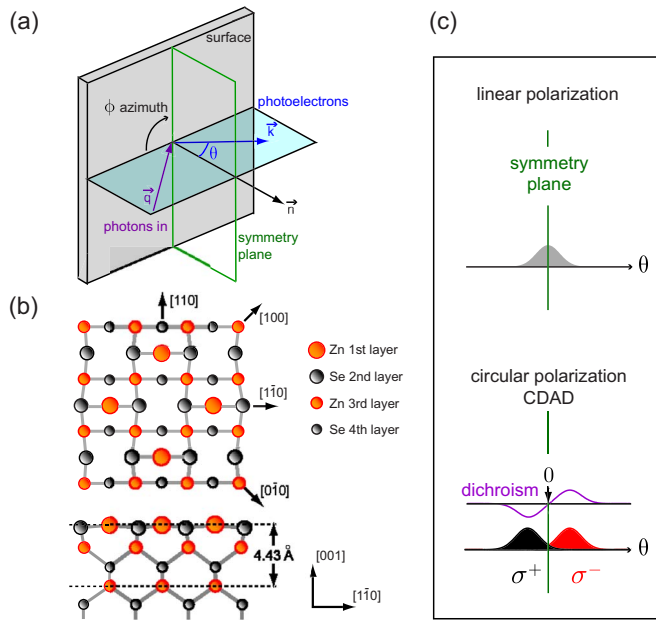


FIG. 1. (Color online) (a) Scheme of the experimental geometry. \vec{q} is the photon wave vector, \vec{k} the electron wave vector, and \vec{n} the surface normal. (b) Ball model of the reconstructed ZnSe(001)- $c(2 \times 2)$ surface, adapted from Ref. 16. (c) Scheme of the photoemission intensity distribution along the polar direction for linear polarization and circular polarizations. In the case of circular polarizations, the resulting dichroism is an odd function of θ when $\theta=0$ corresponds to a symmetry plane.

muths ϕ corresponding to principal directions of the ZnSe $c(2 \times 2)$ -Zn-terminated surface [see ball model in Fig. 1(b)]. When the azimuth ϕ is fixed at a value for which the scattering plane is perpendicular to a mirror plane of the surface, the CDAD vanishes along \vec{n} . Because of the mirror symmetry, $I(\sigma^+, \theta) = I(\sigma^-, -\theta)$, where I stands for the photoemission intensity and the CDAD, defined in what follows as $\text{CDAD}(\theta) = I(\sigma^-, \theta) - I(\sigma^+, \theta)$, is an odd function of θ , as depicted in Fig. 1(c). Therefore, when the azimuth is set to a value corresponding to $[110]$ (mirror plane of ZnSe) the CDAD should be zero at normal emission and should be an odd function of the polar angle for both the surface and bulk components. When the azimuth corresponds to the $[100]$ direction, the scattering plane is not perpendicular to a mirror plane of the surface and, consequently, the CDAD of the surface component is not necessarily odd versus θ .

The situation is different for the bulk components. While the surface has a twofold symmetry, the bulk zinc-blende $F\bar{4}3m$ structure has a fourfold $[001]$ roto-inversion axis. Thus, the CDAD of bulk spectral components should be an odd function of θ for the $[100]$ or $[0\bar{1}0]$ azimuth. In other words, the planes defined by the surface normal and these directions behave like mirror planes of the bulk when CDAD is considered. Such a statement is substantiated by results reported for Si(001). Photoelectron diffraction theory was used by Kaduwela *et al.* to calculate the CDAD from bulk Si(001).⁷ It was shown that most of the CDAD is linked to a helicity-dependent apparent rotation of the photodiffraction

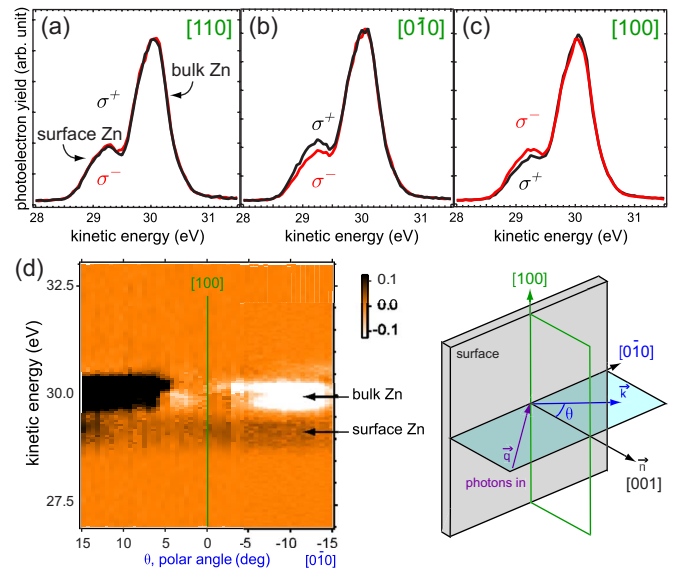


FIG. 2. (Color online) (a) Photoemission spectra collected along the surface normal for the $[110]$ azimuth with σ^+ and σ^- light. (b), (c) Same as (a) but for the $[0\bar{1}0]$ and $[100]$ azimuths. (d) CDAD in the photoemission of Zn $3d$ (excitation energy: 45.5 eV) along the $[0\bar{1}0]$ polar direction for photoelectrons and $[100]$ azimuth, the scheme of the corresponding experimental geometry.

pattern. Therefore, a diffraction feature symmetric with respect to a given azimuth leads to a vanishing dichroism at this particular azimuth. In the case of Si(001), although $([100], \vec{n})$ and $([0\bar{1}0], \vec{n})$ are not mirror planes of the sample, the photodiffraction pattern is symmetric with respect to the $[100]$ and $[0\bar{1}0]$ directions and no CDAD is expected along $[100]$ and $[0\bar{1}0]$.

Summarizing these considerations on symmetry, we expect that the CDAD of the bulk components is an odd function of θ for the $[100]$ and $[0\bar{1}0]$ azimuths, while it is not the case for surface components. In principle, this provides a way to discriminate between surface and bulk components in the photoelectron spectrum.

We first report the data obtained in the Zn $3d$ spectral range. Photoemission spectra collected along the surface normal with σ^+ and σ^- light for the $[110]$, $[0\bar{1}0]$ and $[100]$ azimuths are displayed in Fig. 2(a)–2(c). For the $[110]$ azimuth, both spectra are identical within the experimental error and the dichroism is zero. As mentioned above, this is a consequence from the fact that the plane defined by the $[110]$ direction and \vec{n} is a reflection plane of the crystal and of the reconstructed surface. For the $[100]$ and $[0\bar{1}0]$ azimuths, the bulk component, located at higher kinetic energy around 30 eV, has the same intensity for both polarizations. This contrasts with the sensitivity of the surface component, located at lower kinetic energy, to the helicity of the incoming photons. In this configuration, for photoelectrons emitted along the surface normal, the surface component is dichroic. As neither $([100], \vec{n})$ nor $([0\bar{1}0], \vec{n})$ is a reflection plane of the surface, one expects a nonvanishing dichroism of the

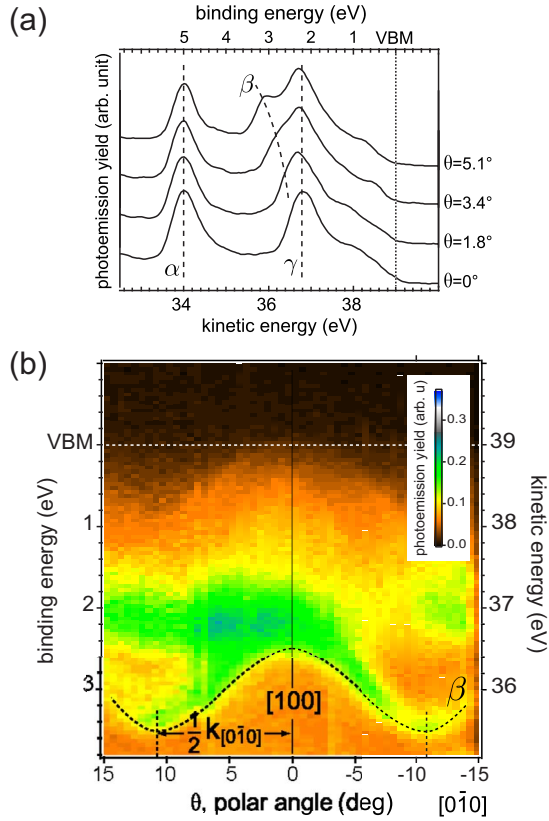


FIG. 3. (Color online) (a) Valence-band photoemission spectra of the ZnSe(001)- $c(2 \times 2)$ surface obtained for [100] azimuth and increasing polar angles with unpolarized light [$I=I(\sigma^+)+I(\sigma^-)$]. The spectra have been smoothed. See text for the discussion about bands labeled α , β , and γ . (b) Polar map of the valence-band photoemission with unpolarized light [$I=I(\sigma^+)+I(\sigma^-)$] for the [100] azimuth. The dispersion of the β component is drawn as the dashed line as a guide for the eye.

surface component even for detection along \vec{n} , as is observed.

The CDAD distribution for ϕ corresponding to the [100] azimuth is displayed in Fig. 2(d). The bulk component is odd against θ , while the surface components do not vanish when $\theta=0$. The CDAD distribution for the [110] reflection direction (not shown) was found to be very weak and vanishes for $\theta=0$, as expected from considerations of symmetry mentioned above. As [100] is not a mirror symmetry direction in the plane of the surface, the CDAD of the surface component does not vanish for $\theta=0$. These observations validate our previous statements on the behavior of the CDAD in connection with the symmetry of the surface and of the bulk.

Thus, these findings suggest a way to discriminate between surface and bulk-related spectral components, based on symmetry arguments: a spectral component that would not be odd against θ for the [100] azimuth must be related to the surface.

It is then interesting to extend the study to the valence band. The surface states of ZnSe are related to the $4p$ orbitals of the Se atoms in the second atomic layer and Zn $4s$ orbitals involving Zn surface atoms, as shown by *ab initio* theoretical calculation by Plucinski *et al.*²¹ The [100] direction is not a

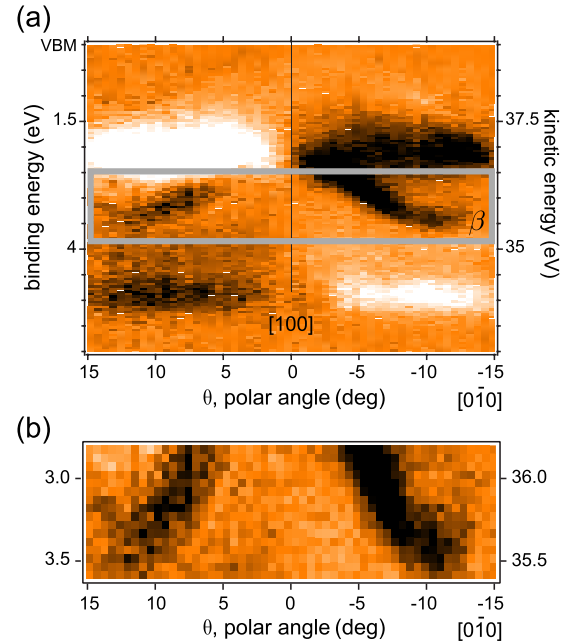


FIG. 4. (Color online) (a) CDAD for the [100] azimuth and polar directions along $[0\bar{1}0]$. The CDAD is an odd function of θ , except for the β component inside the thick gray box. (b) Detailed plot of the CDAD in the spectral region of the β component.

mirror direction for the charge density distribution related to these calculated surface states. Consequently one can possibly identify them using CDAD.

Figure 3(a) shows photoemission spectra of ZnSe valence band recorded for various polar angles with \vec{q} along the [100] azimuth. Three main spectral features can be identified: a nondispersive peak labeled α located at a binding energy of 5 eV, a dispersive feature labeled β between 2.5 and 3.5 eV, and a nondispersive peak labeled γ at 2.2 eV. Plucinski *et al.* identified the nondispersive feature located at 5 eV, lying on the edge of the bulk-projected band structure near the X point, as transitions induced by surface-umklapp scattering via (1,1,0) vectors.²¹ Calculation predicts energy levels at 4.92 eV near the X_{3v} high-symmetry point,²² in good agreement with the value deduced from the spectra. Such transitions were also observed for the Se-rich 1×1 surface and, thus, are not sensitive to the reconstruction. Energy levels at the X_{5v} high-symmetry point are calculated to lie at 2.27 eV (Ref. 22) and observed at ~ 2.1 eV (Ref. 23). These values are in good agreement with the energy of the nondispersive γ feature that we assign to transitions induced by surface-umklapp scattering via (1,1,0) vectors. Concerning the β peak, Xue *et al.* observed surface-related states around 3–4 eV.²⁵ Olgún and Baquero predicted the existence of a dispersive surface cation resonance between 2 eV at the Γ point and 4 eV at the X point,²⁴ but their study dealt with ideally bulk-terminated ZnSe surfaces. The dispersion of the β feature is given in Fig. 3(b). The wave vector component parallel to the surface, k_{\parallel} , is conserved in the photoemission process and is given by $k_{\parallel} = \sqrt{(2m/\hbar^2)E_k} \sin \theta$, where E_k is the kinetic energy of the photoelectrons. Using this relation, it is straightforward to convert the angular range of polar

angles into the k_{\parallel} range in the Brillouin zone (BZ). The $[0\bar{1}0]$ direction corresponds to the Γ - X line in the bulk BZ. The minima in the dispersion of the β component, located at $\theta = \pm 10.5^\circ$ ($\pm 0.2^\circ$), correspond to $k_{\parallel} = 0.56 \pm 0.01 \text{ \AA}^{-1}$. Using the pseudomorphic ZnSe lattice parameter $a_0 = 5.65 \text{ \AA}$, we have $k_{[0\bar{1}0]} = 2\pi/a_0 = 1.11 \text{ \AA}^{-1}$. Thus, the minima in the dispersion of β are located halfway between Γ and X —i.e., at the \bar{J} point of the $\bar{\Gamma}$ - \bar{J} line of the surface BZ for the $c(2 \times 2)$ reconstruction.²¹ As its dispersion has the same periodicity as the surface BZ, the β component can be assigned to a surface-related feature.

The dichroism of the non-surface-specific α and γ components, displayed in Fig. 4(a), is odd against θ and therefore not sensitive to the symmetry of the reconstruction. The situation differs for the β peak as shown in Figs. 4(a) and 4(b) where the CDAD of this component has been enlarged: the dichroism of β is an even function of the polar angle. Considering our previous statements on the parity of the CDAD and its link with symmetry, this behavior is due to the fact

that β is a surface-related spectral feature. As $[100]$ is not a reflection direction of the $c(2 \times 2)$ reconstruction, the CDAD of a surface-related spectral feature is not necessarily odd, contrary to the case of a bulk-related component. This proof-of-principle experiment shows how the CDAD can be used to identify surface bands. This is demonstrated here in a simple case since there is a clear match between the dispersion of β and the periodicity of the surface BZ, but such a behavior is not always observed. It is anticipated that this method can be used to discriminate between bands having more complicated dispersions.

Although the experimental method presented here is relatively complex since it is based on a careful control of the experimental geometry and the availability of circularly polarized light, its principle relies on simple symmetry arguments. Therefore, it should constitute a valuable tool, complementing density functional theory calculations and angle-resolved photoemission with linear polarization, to study the surface band structure of single crystals.

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