Probing two- and three-dimensional electrons in MgB_2 with soft x-ray angle-resolved photoemission

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The electronic band structure of MgB_2 involves a unique combination of two- and three-dimensional (3D) electrons derived from the boron σ and π states, respectively. We have mapped out the σ and π bands over the complete Brillouin zone, including the full disconnected Fermi surface, using high-resolution soft x-ray angle-resolved photoelectron spectroscopy. The measured band structure, which is closely related to that of graphene, is in overall good agreement with the density functional theory–general gradient approximation (DFT-GGA), though differences in Fermi surface volume are seen. Surprisingly, the measured bands are wider than calculated, by $\sim 8\%$ for the σ and $\sim 10\text{--}15\%$ for the π bands. This solves the long-standing challenge of establishing the full 3D electronic structure of the model compound MgB_2 , and it demonstrates the tendency of DFT-GGA to overestimate the band narrowing due to exchange correlations effects.

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I. INTRODUCTION

Magnesium diboride (MgB_2) [1] is a textbook example of a multiband multigap superconductor [2–6] with a critical temperature of $T_c \approx 40$ K, and the pairing due to electron-phonon coupling is understood in great detail [7–9]. Recently, this compound has attracted a more general interest because the honeycomb boron (B) layers are isostructural to the carbon (C) layers of graphene [10], with the two-dimensional (2D) in-plane σ bands playing the essential part for superconductivity in MgB_2 . In addition, the boron π states in MgB_2 form fully three-dimensional (3D) electronic bands disconnected from the 2D σ states. The coexistence of 2D-3D dispersions leads to a particularly interesting dichotomy, which is the focus of this study. The superconducting properties of MgB_2 have been studied extensively using various techniques [11,12]; however, the experimental determination of the electronic band structure and, in particular, its complete 3D Fermi surface (FS) topology are still missing.

Single-crystal bulk measurements using the de Haas–van Alphen (dHvA) technique [13,14] confirmed the existence of all four FS parts presented in the band calculations [15]. However, the experiments [13,14] indicated that FS cross sections showed larger deviations from theory for the σ than for the π bands. Parallel to dHvA, angle-resolved photoelectron spectroscopy (ARPES) is the only experimental technique that can give a direct view of the FS as well as the electronic band structure by supplying detailed information on momentum as well as binding-energy dependence. Until now, published ARPES data from MgB_2 samples [5,6] were of limited quality, and the individual FS sheets and bands could not be clearly distinguished. Furthermore, an extra band centered around the Γ point was detected. This supplementary band was shown to be connected to a magnesium terminated surface state [16].

These complications made data analysis complicated, and a direct comparison with band calculations and with dHvA results is difficult.

Here, we present a high-resolution study of the band dispersions of MgB_2 using the unique capabilities of the soft x-ray ARPES (SX-ARPES) technique. The combination of both 2D and 3D electrons makes MgB_2 an ideal material to be studied by SX-ARPES. In particular, the high k_z -resolution gives direct access to the 3D dispersions [17] as well as intrinsic bulk properties due to the larger escape depth of the SX photoelectrons. The complete 2D and 3D electronic band structure of MgB_2 is revealed with an unprecedented quality, e.g., sharpness of the dispersions and data enhancement were not needed, and in-depth comparison with band calculation is made feasible. The FS topology is in general agreement with calculation, yet clear differences are found in the FS volume. Further, the high-quality data reveal a larger bandwidth for both σ and π bands, which points to the tendency of the density functional theory–generalized gradient approximation (DFT-GGA) method to underestimate the bandwidth. The results highlight the unique power of SX-ARPES for determining the complete electronic band structure of 3D materials, and they exemplify the importance of combining high-quality experimental studies with calculations to obtain a full detailed electronic structure of complex materials.

II. EXPERIMENTS

Data were acquired on the ADDRESS X03MA beamline [18] at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland, employing both linear and circular polarized light at photon energies from 310 to 900 eV, using a PHOIBOS-150 photoelectron analyzer. The energy resolution was set to 70–90 meV and the momentum resolution parallel to the analyzer slit chosen as $\Delta k_{\parallel} \sim 0.01/0.03 \text{ \AA}^{-1}$. The samples were cooled down to $T = 10$ K to suppress thermal broadening, thereby improving the energy resolution. The base pressure of the

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UHV system was below 5×10^{-11} mbar during the entire measurement, and no sign of sample/data quality degradation was observed after cleaving the crystals. The high-quality single crystal MgB_2 samples used in this investigation were grown using a high-pressure technique [19,20], and their quality as well as bulk properties were previously well characterized using a series of experimental methods. We have measured the dispersion along k_z by scanning the photon energy ($h\nu$) at fixed binding energy E_B and emission angle (e.g., $k_{\parallel} = 0$) along the Γ - M (A - L) and Γ - K - M (Γ - H - L) symmetry lines, respectively. The perpendicular momentum k_z is given [21,22] by

$$k_z = \frac{1}{\hbar} [2m_e(h\nu - w_f - E_B + V_0) - \hbar^2(k_x^2 + k_y^2)]^{1/2} + p_{\text{photons}} \sin(\alpha + \phi), \quad (1)$$

where $\hbar$ is the reduced Planck constant, $w_f = 4.5$ eV is the work function, E_B is the binding energy, $V_0 = 15$ eV is the inner potential [4], and $p_{\text{photons}} = h\nu/c$ is the photon momentum. The second term refers to the photon momentum correction needed only at high photon energies, where the photon momentum is large enough to be comparable to the in-plane crystal momentum [23]. The angle $\alpha = 70^\circ$ is the angle between the incident photon beam and the analyzer axis, and ϕ is the polar angle.

III. ELECTRONIC BAND STRUCTURE CALCULATIONS

The electronic band structure calculations were performed using WIEN2K [24] and the generalized gradient approximation by Perdew *et al.* (PBE-GGA) [25]. MgB_2 crystallizes in AlB_2 structure (space group $P6/mmm$) composed of alternating hexagonal layers of boron and magnesium atoms. The calculations were done using the experimental lattice parameters, $a = 3.083$ Å and $c = 3.52$ Å, with internal atomic coordinates determined by total energy minimization. The muffin-tin radii were 2.5 and 1.66 bohr for Mg and B, respectively, and the number of k points in the whole Brillouin zone (irreducible representation) was set to 10 000. The convergence basis set was $R_{\text{mt}}k_{\text{max}} = 7$, where R_{mt} is the smallest atomic sphere radius in the unit cell and k_{max} is the interstitial plane wave cutoff. The angular momentum expansion inside the muffin-tin spheres was $L_{\text{max}} = 5$ for the potential and charge density. Our band-structure calculation agrees well with previous ones [15,26–30].

IV. RESULTS AND DISCUSSIONS

The calculated FS of MgB_2 (Fig. 1) is composed of four sheets: at Γ , two warped cylinders (blue and green) associated with the σ bands and two 3D tubular networks related to the π bonding (orange) and π^* antibonding (red) bands. In Figs. 2(b) and 2(c) we determine the Fermi surface obtained by integrating the photoemission intensity ± 50 meV around the Fermi level (E_F). Data were acquired along two main symmetry planes (shaded area in the schematic Brillouin zone (BZ) [Fig. 2(a)]). Figure 2(b) displays the FS taken along cut where the π bands form disconnected FS pockets centered at M and L , and the σ bands create two warped cylinders along Γ - A . The FS measured along cut [Fig. 2(c)] shows the π

FIG. 1. (Color online) Fermi surface of MgB_2 , composed of four bands, calculated by the density functional theory–generalized gradient approximation (DFT-GGA) method. The green and blue *quasi*-two-dimensional Fermi surfaces are derived mainly from the boron σ bonding bands, while the orange and red three-dimensional Fermi surfaces come from π bonding and antibonding bands, respectively.

band FS pockets touching each other at one point along the K - H line [dashed red and solid orange pockets in Fig. 2(e)]. Both FS measured along cuts and highlight the 3D nature of the π bands, while the σ FS shows a *quasi*-2D character. The π FS measured at M and K are connected to the π bonding band (orange), while the ones centered at L and H are related to the π^* antibonding band (red). Obviously, the 3D nature of the π bands expresses itself in the disconnected parts of the FS, whereas the σ FS (green and blue) are continuous along k_z . Even though the overall features agree well with band calculations, it is interesting to notice that part of the π^* antibonding pocket centered around L is not visible [red dashed line in Fig. 2(c)]. This might be due to a hybridization of the π^* bands causing a loss of photoemission intensity due to matrix element effects. Further studies including polarization analysis are needed to clarify this point.

We now focus on the FS in the k_x - k_y plane at $k_z = 0$ and $k_z = \pi/c$ [Figs. 3(a) and 3(b)]. On both maps, centered around Γ (A) are the two small cross sections of the σ -derived warped cylinders (blue and green)—more visible in the second BZ due to the matrix element effect. Their shape stays similar and only the FS area changes, with the cylinders being narrowest at Γ and widest at A . The large FS is associated with the bonding π and antibonding π^* bands (orange and red). The difference between them is that the π FS is rotated by 30° from the π^* one. All these observations are in line with the k_z FS measurement shown in Fig. 2. Figures 3(c) and 3(d) display the calculated FS at $k_z = 0$ and $k_z = \pi/c$, respectively. While the overall agreement between experiment and calculation is good, particularly concerning the shape, we note that the measured FS cross sections for the π/π^* bands are $\sim 15\%$ larger than the calculated ones.

Next, we discuss the in-plane dispersions $E(k)$ up to ~ 10 eV binding energy. The overall band structure of MgB_2 bears a high resemblance to that of graphene [10] since the boron (B) atoms form a similar honeycomb lattice as do the carbon (C) atoms, and the same σ - π orbitals are involved. Figure 4 displays the electronic band calculation of MgB_2 and

FIG. 2. (Color online) The 3D Fermi surface of MgB_2 measured along two main symmetry planes as indicated in the schematic Brillouin zone (a). (b) Cut 1: The *quasi*-2D σ bands form two warped cylinders along the Γ -A- Γ direction, while the 3D π bands are disconnected pockets centered around M and L . (c) Cut 2: The 3D π bands form irregular Fermi surfaces pockets around M and L that touch each other along the K -H- K line. Both Fermi surfaces were measured in the $(k_x, 0, k_z)$ plane with circular polarized light. The gray scale is linear, with white (black) corresponding to low (high) photoemission intensity. The dashed red line symbolizes the missing part of the pocket (see the text). (d) and (e) Calculated Fermi surface from DFT-GGA along the same cuts.

graphene [10] using the DFT-GGA and Slater-Koster methods, respectively. The topology of both σ and π bands is similar. The main differences, however, result from the band filling, bandwidth, and relative shift of the π bands with respect to

FIG. 3. (Color online) Comparison between measured and calculated Fermi surfaces. Intensity maps measured in the k_x - k_y plane at (a) $k_z = 0$ ($h\nu = 310$ eV) and (b) $k_z = \pi/c$ ($h\nu = 370$ eV). The data were taken with linear polarized light. The quasi-2D σ bands (green and blue) are seen in both maps and keep an identical contour, while one π band (orange) appears at $k_z = 0$, and the other π band (red) at $k_z = \pi/c$ is rotated by 30° . This is in good agreement with the calculation (c,d) reveals differences in the π FS cross sections (see the text).

the σ bands. In MgB_2 , the Dirac point is ~ 1.7 eV above E_F , and the bands are narrower by ~ 12 – 30 % (σ bands) and up to ~ 45 % (π bands). In the entire energy range, Fig. 5 displays sharp and strongly dispersive bands visible in all raw spectra. Studying the bands crossing E_F gives the possibility to discern the hole and/or electron character of

FIG. 4. (Color online) Electronic band structure of MgB_2 and graphene [10]. The topology of both the σ and π bands is similar, only the energy scales and band filling are different.

FIG. 5. (Color online) σ - and π -band dispersions measured along the main symmetry lines using circular polarized light. Spectra (a) and (b) were measured at $k_z = 0$, while spectra (c) and (d) were measured at $k_z = \pi/c$. In all spectra, the σ and π bands cross the Fermi level forming holelike and electronlike Fermi surfaces. The solid blue and red lines represent the DFT-GGA calculated σ and π bands, respectively. Comparison between the measured and the calculated band structure shows that the experimental bandwidth is larger than calculated, where a clear effect is seen at higher binding energy ($E_B \approx 8$ eV) for the M and L points. (e) and (f) Energy distribution curves (EDCs) at $A-L$ and $\Gamma-M$ cuts, respectively. The blue curves are Lorentzian fits of the EDC overlaid on the data (red curves). At the bottom is shown a fit of one of the EDCs, where the green line is the background and the blue dashed lines are the individual Lorentzian peaks. (g) Zoom around the L point at $E_B \approx 8$ eV [dashed yellow box from (c)], and filled circles represent the peak positions obtained from Lorentzian fits to the data. White dashed lines represent a shift of the calculated bands. (h) Same as (g) for the M point.

the four FS pockets at various symmetry points of the BZ. For a detailed comparison between measured and calculated energy bands, we have superposed our band calculation on the as measured ARPES data [solid blue σ and red π bands in Figs. 5(a) and 5(d)]. Although the overall agreement between the experimental results and calculations is good, differences can be noticed, particularly for the π bands. At L , the measured electron pocket has a smaller FS cross section (by $\sim 10\%$) than what is estimated by calculation [Fig. 5(c)]. This is consistent with the in-plane FS area shown in Fig. 3, as mentioned above. To correct for this, the calculated antibonding π^* band would have to be shifted by approximately 200 ± 50 meV toward E_F .

In the following, we discuss in quantitative detail the width of the individual bands. Motivated by the interesting observation made in graphite [31–33], where the comparison between band calculation and measurement of the bandwidth revealed small but significant differences, we analyze in the same spirit several of the bands in MgB₂. For the σ bands, the calculation gives a width that is $\sim 8\%$ smaller in the $A-L$ than in the $\Gamma-M$ direction. The experiment, however, shows the same bandwidth for both of these direction, and it is 1–2 % wider than the calculated one along $\Gamma-M$. For the π bands, the measured width for the band dispersing from L to H to A [Fig. 5(d)] is ~ 10 –15 % larger than the calculated one. Such an underestimation of the calculated bandwidth is reminiscent and in quantitative agreement with earlier results on graphite [31,32], where this systematic discrepancy was ascribed to the degree that exchange correlation effects are included in the calculation. The effect of the dynamic exchange correlation potential, related to the self-energy, is considered in [31,32] and found to be different from the static density functional theory–exchange correlation potential. This self-energy correction is related to the spatial localization of the wave functions, and it differs for the σ and π states. However, Ref. [32] compares only the σ and π bands along the $\Gamma-A$ direction. While the energy of these two particular points is better represented by the GW approximation, it is not clear if it is due to a modification of the overall bandwidth or shift of the bands. Similarly, the most recent and high-quality study on graphite [33] is focused on the $K-H$ points, where the GW approximation described better the dispersions close to the Fermi level. A comparison between band calculation and experiment for the overall band structure was not yet done.

Given these bandwidth differences, it is not surprising to find notable effects near the edge of the bands, in particular near the Fermi level, e.g., close to the top of the σ bands or the gap deep in the band at the L and M points around 8 eV. Figure 5(g) shows an expanded view of the data in Fig. 5(c) (yellow dashed rectangle) at the L point with the corresponding DFT-GGA calculation overlaid. A shift of the calculated bands edges by approximately 0.6 eV is needed in order to fit the data as indicated by the small white arrow and dashed white lines. The high data quality further allows for a more quantitative parametrization by performing fits of the energy distribution curves (EDCs) using resolution broadened Lorentzian functions describing the intrinsic lifetime. The lifetime was estimated from the bandwidth away from the gap region. As shown in Fig. 5(e), the EDCs display two distinct peaks approaching each other at $E_B = 8$ eV. By overlaying the peak positions (filled circles) obtained from the EDC

fits onto Fig. 5(g), the experimental gap is determined as $\Delta_{\text{exp}}^L \approx 0.9 \pm 0.1$ eV, thus slightly bigger than predicted by DFT-GGA ($\Delta_{\text{DFT}}^L \approx 0.6$ eV). By performing a similar analysis also at the M point, we instead find [Figs. 5(f) and 5(h)] that the experimental gap $\Delta_{\text{exp}}^M \approx 0.4 \pm 0.2$ eV is slightly smaller than the calculated $\Delta_{\text{DFT}}^M \approx 0.7$ eV.

Focusing now on the Fermi surface cross sections, we note that both dHvA [13,14] and our ARPES data reveal differences between measurements and calculations. In this study, we found that the deviations are more pronounced for the π bands, while for dHvA [13,14] the σ bands show more dissimilarities. This might be caused by slight variations of the Fermi level due to differences in the stoichiometry.

Finally, we should also mention that none of our measurement indicates any signature of a surface state at variance with previous low-energy studies [5,6]. This not only confirms the origin of this band, but it also highlights the fact that SX-ARPES is indeed a technique that gives access to the intrinsic *bulk* electronic structure.

V. CONCLUSIONS

To summarize, we performed high-resolution SX-ARPES measurement on MgB_2 single crystals as a function of photon

energy, and we established its full 3D electronic band structure. Analyzing the data near the Fermi level, we observed a clear 3D disconnected Fermi surface (FS) related to the boron π bands and a *quasi*-2D FS associated with the σ bands. The Fermi surface topology is in overall agreement with DFT-GGA band calculations, yet we find deviations for the Fermi surface cross sections and bandwidth for both σ and π bands. We compared MgB_2 with graphite as both compounds include the same honeycomb network of B and C, respectively, and thus the similar σ - π derived band structure. Our results clearly demonstrate how powerful the SX-ARPES technique is to probe the bulk bands of 3D compounds, and they provide an example of the detailed insight into the electronic structure of advanced materials that can be gained by combining state-of-the-art experimental and computational methods.

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