Spin-resolved photoemission of a ferromagnetic Mn_5Ge_3(0001) epilayer on Ge(111)

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Abstract

Here we present a study of the electronic structure of epitaxial ferromagnetic Mn_5Ge_3(0001) films on Ge(111) by means of x-ray absorption spectroscopy, x-ray photoelectron spectroscopy, and spin-resolved photoelectron spectroscopy. Spin-polarization (P) value of $+(15 \pm 5)\%$ at the Fermi energy (E_F) is measured with a photon energy of $h\nu = 21.2\,\text{eV}$. Our findings are in contrast to recent band structure calculations predicting $P = -41\%$ at E_F for the ferromagnetic bulk Mn_5Ge_3.

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I. INTRODUCTION

In spintronics both charge and spin degrees of freedom are exploited in the same material in order to create a future generation of devices being smaller, more versatile and more robust than those currently used in conventional silicon-based circuit elements. The spin transistor together with the underlying basic concept of spin injection is one of the possible applications in this field. The first theoretical demonstration of the spin field effect transistor was given by Datta and Das in 1990 [**?**]. However this concept has not yet been realized in experiments, mainly because it requires spin injection from a ferromagnetic metal (for example Fe) into a semiconductor which has been shown to be practically impossible due to the large conductivity mismatch between a metal and a semiconductor [**?**]. This situation can be improved by the preparation of epitaxial ferromagnetic compounds on the basis of $3d$ metals and silicon or germanium grown on the semiconducting substrates. Among them Mn-based materials are most promising candidates because the Curie temperature of corresponding silicides or germanides can reach room temperature [**?**]. Recently, the preparation of epitaxial Mn_5Ge_3(0001) films on a Ge(111) substrate together with the investigation of crystallographic structure as well as magnetic, electronic and transport properties have been reported in a series of subsequent works [**? ? ? ? ?**]. Point-contact Andreev reflection (PCAR) measurements on the Mn_5Ge_3 epilayers revealed a spin polarization value of $P_{PCAR} = 42 \pm 5\%$ which is close to the calculated spin polarization in the diffusive limits [**? ?**].

Here we present a study of the electronic structure of high-quality epitaxial ferromagnetic Mn_5Ge_3(0001) films on Ge(111) by means of x-ray absorption spectroscopy (XAS), x-ray photoelectron spectroscopy (XPS), and spin-resolved photoelectron spectroscopy (SRPES). The spin-polarization value of about $+(15 \pm 5)\%$ is measured at the Fermi level thus showing an opposite sign compared to the one calculated for bulk Mn_5Ge_3. The experimental photoemission data are discussed in the light of the available band structure calculations for ferromagnetic bulk Mn_5Ge_3.

II. EXPERIMENTAL DETAILS

Photoemission experiments were performed at about 190 K in the experimental setup for SRPES described in detail elsewhere [?]. All spectra were collected in the angle-integrated mode with an acceptance angle of about $\pm 6°$. The energy resolution was set to 100 meV and 500 meV for photoemission studies of the valence band (He Iα,$h\nu = 21.2$ eV; He IIα,$h\nu = 40.8$ eV) and core-levels (Al Kα, $h\nu = 1486.6$ eV), respectively. Spin-resolved spectra were measured in remanence. The samples were magnetized in the direction marked by a white arrow in Fig. 1(b) which corresponds to the $< 1\bar{1}0 >$ direction of bulk Ge. The experimental setup asymmetry was corrected via measurements of two spin-resolved spectra for two opposite magnetization directions of the sample [? ?]. The base pressure in the experimental station is 5×10^{-11} mbar, rising to 8×10^{-10} mbar during metal evaporation. The cleanliness of the samples was monitored by XPS of core levels and photoemission of the valence band. XAS, XPS, and resonance photoemission studies were performed at the D1011 beamline of the MAX-lab synchrotron facility (Lund, Sweden) in total electron yield mode (TEY) with an energy resolution of 200 meV.

III. RESULTS AND DISCUSSION

Prior to the Mn_5Ge_3 film preparation, the surface of the Ge(111) sample was cleaned by Ar^+-ion sputtering and annealing at 650 K until a clear $c(2 \times 8)$ reconstruction pattern was observed by low-energy electron diffraction (LEED) [Fig. 1(a)]. Mn_5Ge_3 films were grown by the deposition of Mn (50 Å, 100 Å, 150 Å, and 200 Å) on Ge(111) at about 190 K and a subsequent annealing at about 700 K for 10 minutes. The surface of the prepared Mn_5Ge_3 film always displays a structural ordering corresponding to the $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction with respect to the (1×1) bulk-derived Ge(111) structure [Fig. 1(b)]. The corresponding crystallographic arrangement of the $Mn_5Ge_3(0001)$ layer on the Ge(111) surface is shown in Fig. 1(c). According to the crystallographic structure two terminations of the $Mn_5Ge_3(0001)$ surface are possible: Mn or mixed Mn/Ge. However by comparison of scanning tunneling microscopy data with density-functional theory calculations it has recently been shown that only simulated Mn-terminated surface fits well the experimental results [?].

Figure 2(a) shows an x-ray diffraction (θ-2θ) pattern of an epitaxial Mn_5Ge_3 film obtained after annealing of 200 Å of prediposited Mn on Ge(111). The XRD pattern is that expected for the diamond structure of Ge showing (hhh) reflections of the Ge(111) substrate. In addition Mn_5Ge_3 (002) and (004) hkl reflections were observed. As expected for this system the hexagonal (0001) basal plane of Mn_5Ge_3 matches well the Ge(111) substrate [**?**].

Magnetic properties of the samples were studied by means of superconducting quantum interference device (SQUID) magnetometry. Fig. 2(b) shows a typical in-plane magnetization of the Mn_5Ge_3 film, obtained after annealing of 200 Å of prediposited Mn on Ge(111), measured as a function of temperature in an applied field of 150 mT in zero-field cooled (ZFC) and field-cooled (FC) conditions. Both $M(T)$ curves reveal a ferromagnetic behavior with T_C at about 300 K being in good agreement with the previous studies [**?**]. An additional feature starting at about 75 K is visible in both measurements, which is absent in bulk Mn_5Ge_3 [**?**]. A small divergence of ZFC and FC measurements on the Mn_5Ge_3 sample starting at 75 K can be attributed to a blocking process of moments of superparamagnetic Mn_5Ge_3 nanoparticles incorporated into Ge matrix most possibly at the Mn_5Ge_3/Ge interface. These particles have moments that are blocked progressively with decreasing temperature, giving rise to the observed irreversibility (difference between FC and ZFC). Magnetic hysteresis loops at 20 K and 300 K [see inset in Fig. 2 (b)] show typical features of ferromagnetic ordering, with a coercive field of $\approx$ 60 kA/m at 10 K.

Fig. 2(c) and (d) show Ge $3p_{3/2,1/2}$ XPS as well as Mn $L_{2,3}$ XAS spectra of the epitaxial Mn_5Ge_3(0001) film obtained after annealing of 150 Å of prediposited Mn on Ge(111), in comparison with the XPS spectra of the clean Ge(111)-$c(2 \times 8)$ surface and with XAS spectra of a thick Mn metal film, respectively. After formation of the Mn_5Ge_3 alloy the Ge $3p$ emission spin-doublet is shifted to lower binding energies (BE) by $\approx$ 0.5 eV due to the larger electronegativity of Ge compared to Mn. The Mn $L_{2,3}$ XAS spectrum of the Mn_5Ge_3 alloy is close to those measured on metallic Mn [see Fig. 2(d)] and on MnSb as well as Heusler alloys [**?**] with two broad spin-orbit split lines. The absence of a fine structure due to the $2p^5 3d^6$ final state multiplet is assumed as an evidence of more delocalized magnetic moments on Mn lattice sites [**?**]. The XPS Mn $2p$ spectrum of Mn_5Ge_3 (not shown here) is similar to that of pure Mn showing no evidence for the atomic-like structure of multiplet-split states or the charge-transfer related satellites detected in diluted magnetic semiconductors [**?**]. The previous works on some of Heusler-alloy compounds show that even for the ferromagnetic materials the line-shape of the Mn $2p$ XPS and XAS spectra can have a Mn-metal like shape [**?**], similar to our observation. However, LEED, XRD, and SQUID results confirm the formation of the ordered ferromagnetic Mn_5Ge_3(0001) epitaxial layer on Ge(111) excluding the presence of metallic Mn in the system.

The spin-resolved and spin-integrated electronic structure of Mn_5Ge_3(0001) films on Ge(111) was studied by means of photoelecron spectroscopy of the valence band with He Iα and He IIα resonance lines at 190 K. The Mn_5Ge_3 films obtained after annealing of 150 Å of prediposited Mn on Ge(111) were used in photoemission experiments. The results of these studies are presented in Fig. 3, showing a spin-resolved photoelectron spectrum of the Mn_5Ge_3 film (a) together with the corresponding spin polarization [inset in Fig. 3 (a)] as a function of binding energy measured with 21.2 eV; valence band spectra of the Mn_5Ge_3 film (b) measured in normal emission geometry and in angle integrated mode with 21.2 eV as well as 40.8 eV; and part of the spin-resolved band structure of bulk Mn_5Ge_3 along the $\Gamma - A$ direction (c) [**?**].

The spin-integrated spectra of Mn_5Ge_3(0001) in Fig. 3(b) show several photoemission features: the first one (A) is located at the Fermi level (E_F) and two additional features are centered at $\approx$ 3 eV (B) and $\approx$ 5.5 eV (C). The first two features are close to those observed for the metallic Mn but slightly shifted in energy due to hybridization with Ge. The last feature (C) does not correspond to any features observed for Ge(111) and is thus characteristic for the Mn:Ge phase in agreement with the previous observations [**?**].

SRPES spectrum of the Mn_5Ge_3(0001) epilayer measured in the angle-integrated mode at 190 K is shown in Fig. 3(a). Intensities of spin-up ($I_\uparrow$) and spin-down ($I_\downarrow$) photoemission channels as a function of binding energy are shown by closed triangles-up and open triangles-down, respectively. The corresponding spin polarization calculated as $P = (I_\uparrow - I_\downarrow)/(I_\uparrow + I_\downarrow)$ is shown by solid squares in the inset. Several distinct features can be identified in the spin-resolved spectra. For the spin-up channel they are: a peak at 0.22 eV, a shoulder centered at 0.87 eV, and a broad maximum centered at 2.84 eV of BE. For the spin-down channel they are: broad maxima located at 0.38 eV and 2.52 eV (with higher BE tail) of BE. The respective spin-polarization calculated from experimental data shows a clear variation as a function of BE and reach the maximum value of about $+(15 \pm 5)\%$ at the Fermi level. However, this value as well as the sign of spin polarization are different from the value of -41% calculated for bulk Mn_5Ge_3 [**?**].

Available band-structure calculations of the bulk Mn_5Ge_3 crystal were used for the interpretation of the obtained experimental results [? ?]. The detailed features in the spin-resolved photoemission spectra of Mn_5Ge_3(0001) epilayer are compared with the band dispersion in the $\Gamma - A$ direction [Fig. 3(c)] as calculated in Ref. [?]. For the final state in the photoemission we assumed a free-electron-like dispersion with a spin-averaged inner potential in the range of $3.5 - 4.5$ eV. The downshift of the final-state dispersion by 21.2 eV leads to the crossing points with the spin-split conduction bands in the region of wave vectors ranged by dashed lines in Fig. 3(c), which can be related to the features in the spin-resolved photoemission spectra. (An additional error in the interpretation is introduced by the broad region of component of wave vector parallel to the surface due to the angle-integration of about $\pm 6^\circ$ in spin-resolved measurements). The calculated band structure shows energy dispersions that are drastically changed upon going from the Γ point to the A point. As stated in Ref. [?] the change of the lattice constant of Mn_5Ge_3 used in the calculations leads to drastic changes in the calculated spin polarization indicating a surprisingly large sensitivity of the polarization to the details of the crystal structure that was assigned to the complicated Fermi surface of this material. For better interpretation of the obtained results the spin-resolved calculations for the (0001) surface of Mn_5Ge_3 are desirable.

In conclusion, the electronic structure of the high-quality ferromagnetic epitaxial Mn_5Ge_3(0001) thick film grown on Ge(111) was studied by means of XPS, XAS, and spin-resolved photoemission of the valence band. A spin-polarization value of about +15% is found at the Fermi level. These results are discussed in the framework of available calculated band structure.

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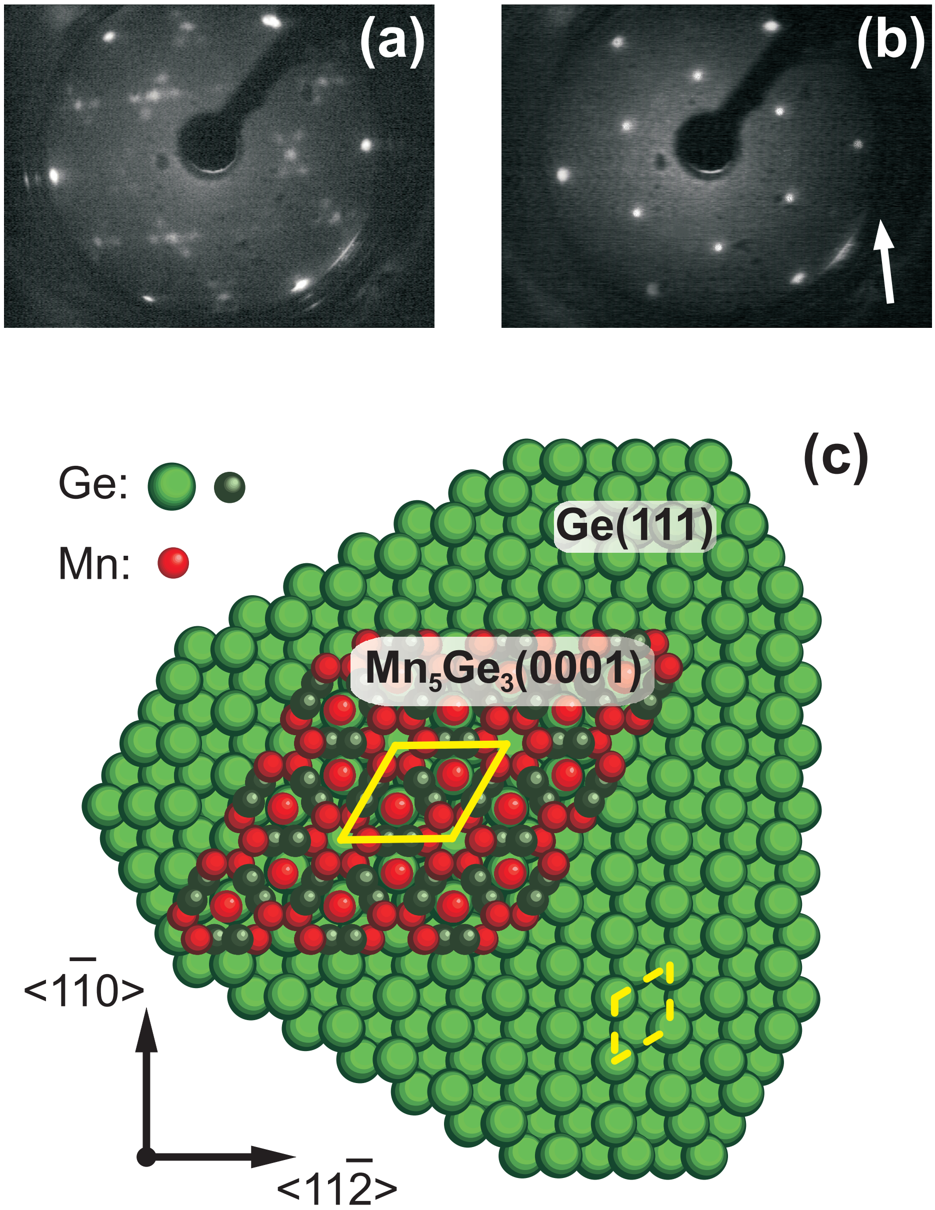
Figure captions:

Fig. 1. (Color online) LEED images (a) of the clean Ge(111) $- c(2 \times 8)$ surface and (b) of the $Mn_5Ge_3(0001) - (\sqrt{3} \times \sqrt{3})R30^\circ$ thick film. (c) Schematic representation of the corresponding crystallographic arrangement of a $Mn_5Ge_3(0001)$ layer on the Ge(111) surface. The respective unit cells are marked in the figure by white rhombuses. Marked crystallographic directions are referenced to bulk Ge.

Fig. 2. (Color online) (a) An x-ray diffraction (θ-2θ) pattern of the epitaxial Mn_5Ge_3 film on Ge(111) (the peak marked with asterisk is related to Cu capping layer deposited for *ex situ* measurements); (b) The temperature-dependent magnetization $M(T)$ measured in a 150 mT magnetic field under field cooled (solid circles) and zero-field cooled (open circles) conditions. The inset represents magnetic hysteresis loops of the $Mn_5Ge_3(0001)$ sample measured at 10 K and 300 K. In (c) XPS spectra of the clean Ge(111) $- c(2 \times 8)$ surface as well as of the $Mn_5Ge_3(0001) - (\sqrt{3} \times \sqrt{3})R30^\circ$ thick film are shown. (d) XAS spectrum of the same $Mn_5Ge_3(0001)$ film as compared to that of a thick bulk-like Mn film.

Fig. 3. (Color online) (a) Spin-resolved photoelectron spectra and corresponding spin polarization (inset) as a function of binding energy of the valence band of the $Mn_5Ge_3(0001)$ thick film measured with 21.2 eV. (b) Valence band spectra of the same film measured in normal emission geometry and in angle-integrated mode with 21.2 eV and 40.8 eV photon energies. (c) Part of the spin-resolved band structure of bulk Mn_5Ge_3 along the $\Gamma - A$ direction for spin-up and spin-down electrons [**?**].



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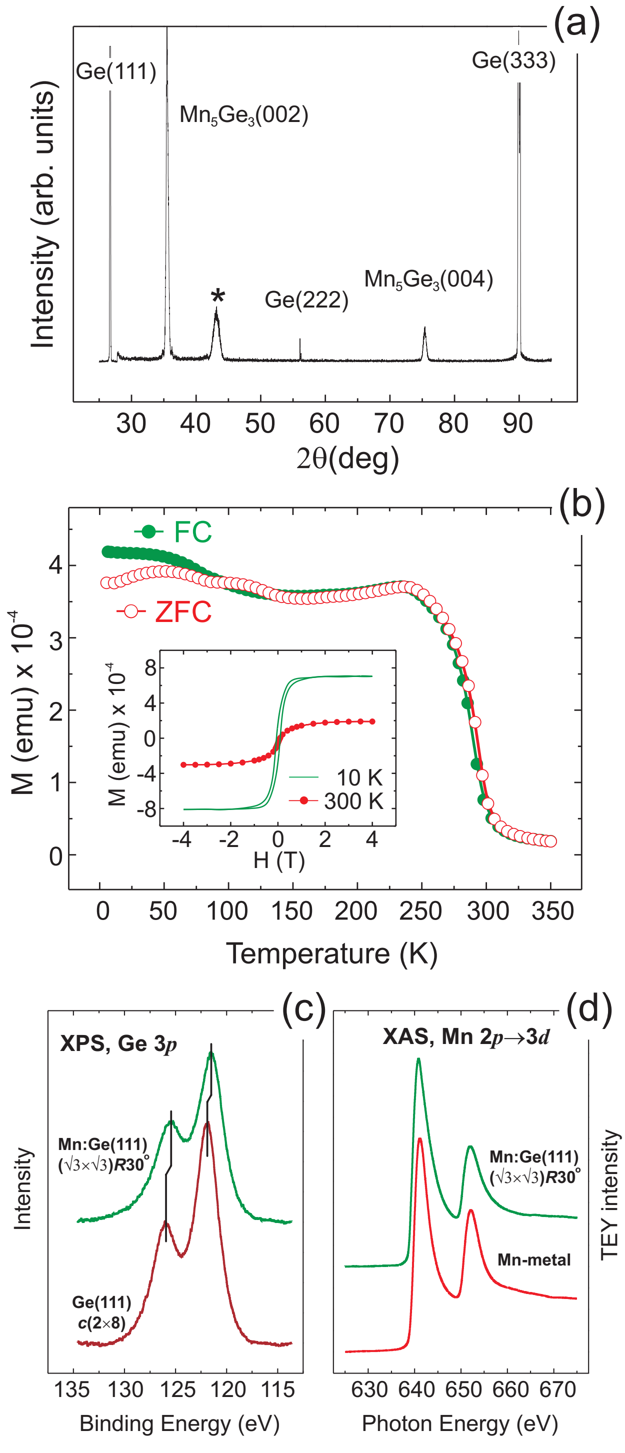

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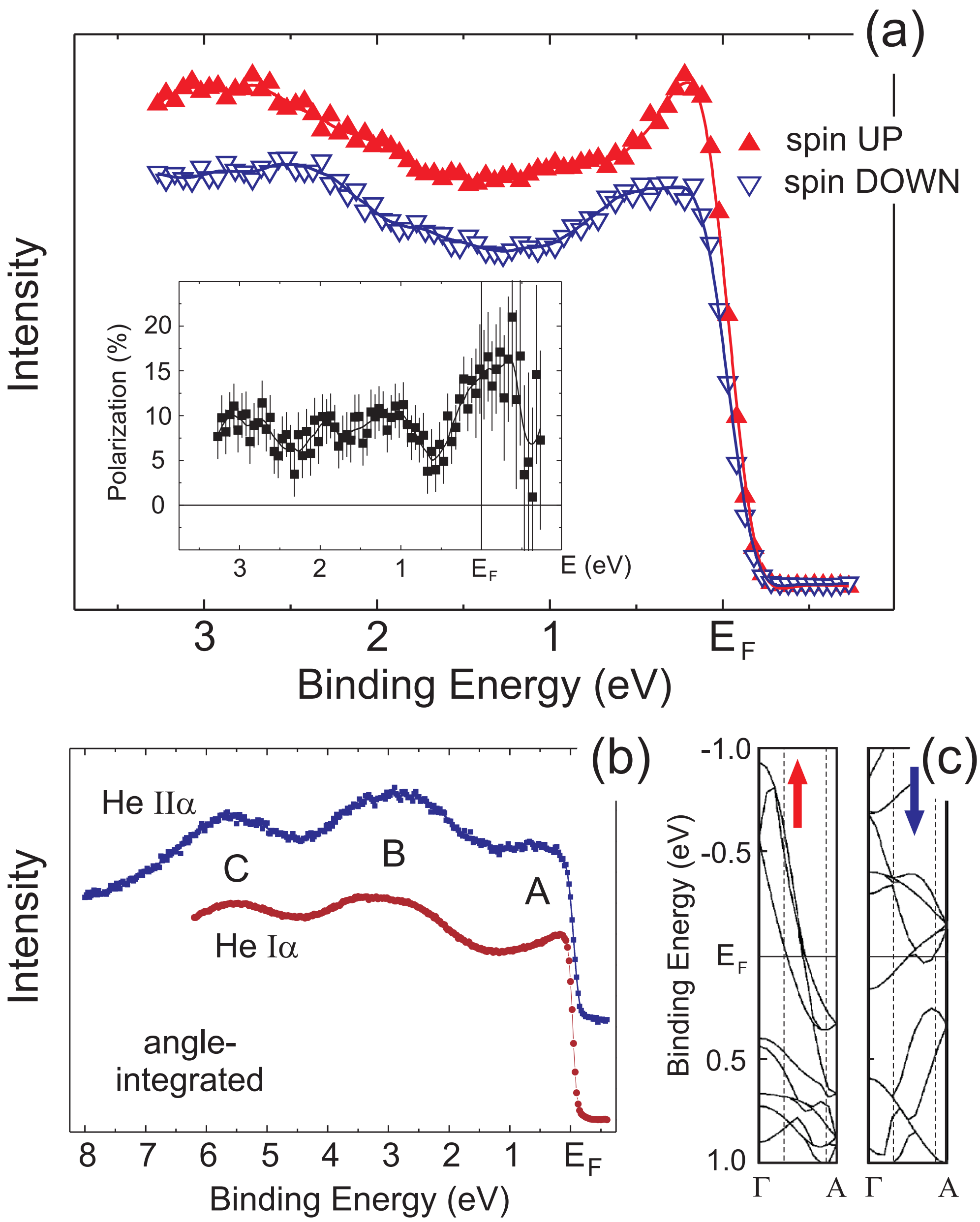

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