Identifying the Electronic Character and Role of the Mn States in the Valence Band of (Ga,Mn)As

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We report high-resolution hard x-ray photoemission spectroscopy results on (Ga,Mn)As films as a function of Mn doping. Supported by theoretical calculations we identify, for both low (1%) and high (13%) Mn doping values, the electronic character of the states near the top of the valence band. Magnetization and temperature-dependent core-level photoemission spectra reveal how the delocalized character of the Mn states enables the bulk ferromagnetic properties of (Ga,Mn)As.

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Understanding the electronic and magnetic properties of diluted magnetic semiconductors has been a major challenge in materials science over the last decade, and carrier-mediated ferromagnetism is undoubtedly one of the most discussed issues in diluted magnetic semiconductor research [1–6]. The case of the (Ga,Mn)As valence band is prototypical: Whether the states near the Fermi level, $E_F$, are best described in terms of dispersive states fully merged with the GaAs valence band or if these states preserve the character of an impurity band has been a subject of intense activity in solid-state science [3–6]. Both descriptions stand on experimental and theoretical arguments that favor one or the other vision [5–9], and more recently unified pictures have been presented [10–13]. Nonetheless, the crossover regime between impurity states at low doping and extended states at high doping, i.e., the essence of how ferromagnetism is established in (Ga,Mn)As, is far from a unified and clear description. Such a description is intimately linked to a further central question: how important is localization vs hybridization of carriers in the vicinity of $E_F$ as a function of doping? Theoretical modeling has so far only offered an inconclusive contribution to this issue, since disorder and strong electronic correlations render realistic calculations difficult to perform. On the experimental front, full control of the system is hard to achieve and a limited number of direct measurements of the (Ga,Mn)As valence band have been reported [14–18].

The need to overcome the solubility limit to obtain stable ferromagnetic order strongly influences the homogeneity of (Ga,Mn)As, thus producing e.g., a depletion zone near the interface accompanied by a strong reduction of the Curie temperature, $T_C$ [19], and a profound difference between surface and bulk electronic properties [7,19].

In the present work, we exploit bulk-sensitive hard x-ray photoemission spectroscopy (HAXPES), corresponding to a severely suppressed (< 4%) surface contribution [20,21], where the combined measure of valence band and core level, including temperature-dependent core-level magnetic circular dichroism (MCD), allows a direct determination of the bulk density of states near $E_F$ as a function of Mn doping. Supported by theoretical calculations, we observe that (i) a clear density of states (DOS) with Mn $3d$ character is present, starting at a Mn doping level as low as 1%, (ii) the Fermi energy is located well above the GaAs host valence band top, and (iii) the delocalized character of the Mn states has a direct link with the (Ga,Mn)As ferromagnetic properties.

We have studied three (Ga,Mn)As thin films (Mn 1%, 5%, and 13% doping, 18–50 nm of thickness). HAXPES measurements were carried out at SPring-8 (Japan) using linearly polarized x rays on beam line BL15XU and circularly polarized x rays on beam line BL47XU. The overall
energy resolution was set to 250 meV for core level and 150 meV for valence band experiments, as verified by measuring the Au valence band from a polycrystalline sample in thermal and electrical contact with the (Ga,Mn)As sample. Further details concerning the photoemission measurements, sample growth and characterization, and calculation methods can be found in Ref. [22].

In Fig. 1 we show successive images of the valence-band region of pure GaAs and Mn-doped samples, with increasing magnification of the near $E_F$ zone. Experimental results [$h\nu = 5953$ eV, Figs. 1(a)–1(c)] are compared with the theoretical curves [Figs. 1(d)–1(f)] based on a one-step model of angle-integrated photoemission. For the sake of comparison, the GaAs spectra have been aligned to the (GaMn)As spectra using the binding energy (BE) position of the As 4s core level. The electronic structure calculations used for the one-step photoemission intensities are based on the fully self-consistent combination of density-functional theory, the coherent-potential approximation to describe the presence of the Mn dopant, and dynamical-mean-field theory (DMFT) as implemented within the multiple scattering Green’s function formalism [23–27].

The self-energy is instead obtained by means of the exact diagonalization solver as in Ref. [12]. The calculations agree quantitatively with the experimental data over a wide BE range. The As 4s states are located at $\sim 10$ eV BE and their effective hybridization with the Mn 3d states is small as they are well separated in energy [Figs. 1(a)–1(d)]. Closer to $E_F$, the Mn 3d states of $e_g$ symmetry hybridize weakly with a mixture of As 4p (mainly) and Ga 4p states. Instead, the Mn 3d states of $t_{2g}$ symmetry exhibit a more significant hybridization just below $E_F$. In Fig. 1(e), high-resolution spectra measured in the vicinity of $E_F$ are displayed for pure GaAs, 1% and 13% Mn doping. Also shown are the difference spectra, where the pure GaAs spectrum is subtracted from the 13% and 1% Mn spectra (orange and grey, respectively), in order to highlight the Mn contribution. In Fig. 1(f), the calculated difference spectra, GaAs subtracted from (GaMn)As, are presented for the local density approximation (LDA) and DMFT calculations (violet and green curves, respectively).

The spectral weight of the difference spectra in Fig. 1(c) is peaked at $\sim 200$ and $\sim 250$ meV below $E_F$ for a Mn

![FIG. 1 (color online).](image-url)

(a)–(c) HAXPES spectra ($h\nu = 5953$ eV) for different Mn doping in GaAs. The GaAs spectra have been aligned to the (GaMn)As spectra using the BE position of the As 4s core level. No background subtraction was applied. (a) Extended valence band PES ($T = 20$ K), including the As 4s, Ga 4s, and As 4p shallow core levels of GaAs(100) and 13% Mn-doped GaAs. (b) Zoom of the valence band region ($T = 100$ K), showing the spectra from pure GaAs (black dots), 1% and 13% Mn-doped GaAs (red and blue dots, respectively). (c) High-resolution spectra measured in the vicinity of $E_F$. Difference spectra, corresponding to the Mn contribution only, are shown in orange [13% Mn spectrum (blue dots) minus pure GaAs spectrum (black dots)] and grey [1% Mn spectrum (red dots) minus pure GaAs spectrum (black dots)]. The reference Fermi level of Au is displayed, offset. (d) Calculated angle-integrated PES (including matrix elements) for photon energy and geometry ($p$ polarization) as used in the experiment. (e) Calculated valence-band spectra of GaAs(100) using LDA (black curve) and (Ga,Mn)As (13%) using both LDA (red curve) and DMFT (blue curve). (f) Zoom of the vicinity of $E_F$ with calculated difference spectra, as in (c), for LDA (violet curve) and DMFT (green curve).
content of 1% and 13%, respectively, in agreement with previous photoemission results [11,14,16]. The LDA calculation in Fig. 1(f), instead, exhibits a broad plateau, leading into poor agreement with experimental data. This agreement improves in LDA + DMFT, where a well-defined peak forms, but centered at ~500 meV. From the calculations we infer that the maximum in the difference signal has mainly a Mn-3d \( t_{2g} \) character. A strong hybridization is present with a mixture of mainly As 4p states localized around the impurity, and Mn 4p states. Therefore we identify the approximate treatment of this hybridization, which is inner to the exact diagonalization solver, as the main reason of the discrepancy in the peak position. It is important to emphasize that the Mn-related DOS near \( E_F \), although significantly smaller, is nonzero within the energy resolution. The diluted nature of Mn in the host GaAs matrix is confirmed by the spectroscopic fingerprint of the difference spectra in Fig. 1(c): the Mn states in (Ga,Mn)As retain their Gaussian line shape (broadened when the doping value increases) up to a Mn doping as high as 13, whereas for MnAs, a truly metallic system, one obtains a clear Fermi edge [22].

Having ascertained the nature and evolution of the Mn states in the vicinity of \( E_F \), we now use circularly polarized x rays (MCD-PES) to have access to magnetic information [28,29]. Figure 2 shows the core-level HAXPES \((h\nu = 7940 \text{ eV})\) for a 13% Mn-doped GaAs sample in the ferromagnetic state (below its Curie temperature, \( T_C = 80 \text{ K} \)), and compared to model calculations. Figure 2(a) shows a survey spectrum that identifies the Mn 2p doublet with the well-screened and poorly screened features of the 2p\(_{3/2}\) and 2p\(_{1/2}\) core levels, in agreement with previous results [28,29]. Figure 2(b) shows the MCD for the full Mn 2p region, with a very large magnetic asymmetry of ~13%. The line shape of the Mn 2p core level does not change while varying the Mn concentration from 1% to 13%, which is strong evidence against an important contribution of interstitial Mn atoms in our bulk-sensitive spectra [28]. The calculations in Fig. 2(c), using the Anderson impurity model [22], shows that the 2p\(_{3/2}\) structure contains a well-screened peak at the high kinetic energy (low BE) side and a poorly screened peak at 1–2 eV lower kinetic energy (higher BE), with opposite dichroism [28,29]. The well-screened peak is found to have mainly \( 2p^23d^5h^2 \) character, while the poorly screened peak has mainly \( 2p^23d^5h^2 \) character, where \( h \) denotes a hole state. In the ground state, the 3d\(^5\)h state is pinned to \( E_F \), and it is the 3d\(^5\)h\(^2\) state that is pulled down in energy in the final state due to the 2p core-hole potential [28]. In the calculation, the local ground state properties are primarily reflected by two parameters: The transfer integral \( V \) responsible for the hybridization (mixing) and the on-site 3d electron-repulsion energy \( U \), i.e., the Hubbard \( U \). The experimental MCD of the HAXPES agrees very well with the calculated spectra for a hybridization parameter \( 2.0 \leq V \leq 2.5 \text{ eV} \). The most intense magnetic signal, corresponding to the leading well-screened peak, is linked to the most delocalized electronic \( d \) character, an attribute already put forward by the results of Dobrowolska et al. [30] and in good agreement with Richardella et al. [13].

Additional evidence of the role played by the electron hybridization of the Mn 3d states is obtained from
temperature-dependent HAXPES. Knowing that the carrier concentration in a heavily doped semiconductor, such as (GaMn)As, does not change significantly with temperature [30], a shift of the core levels and/or the valence band spectra vs temperature is associated with a change in the screening efficiency of the delocalized electrons. The HAXPES results are shown in Fig. 3 (13% Mn doping); while the Ga $2p$ peak shifts $\sim 80$ meV to higher BE between 20 K and room temperature, the measured valence-band shift is less than 40 meV. This temperature dependence implies an increased Mn $3d$-$As 4p$ hybridization, and hence a more efficient hopping favoring ferromagnetism [28–32]. Moreover, the low BE feature of the Mn $2p_{3/2}$ core level (associated with the more delocalized $d^6h^2$ states) shifts with temperature by $\sim 35$ meV, whereas no shift of the broad component at higher BE (corresponding to the more localized $d^3h$ states) is detected.

This observation confirms that the screening is associated exclusively to the more hybridized Mn $3d$ states, $d^6h^2$, while the localized $d^3h$ states, near $E_F$, do not participate in the screening process. A further confirmation of this picture comes from the calculated MCD-PES in Fig. 2(b), where the energy separation between the sharp negative peak and broad positive peak in the Mn $2p_{3/2}$ increases with $V$; this again implies a more efficient screening due to delocalized electrons.

The physical scenario emerging from our combined observations and calculations is presented in Fig. 4. The GaAs valence band is substantially modified by the introduction of Mn atoms, even for doping values as low as 1%. The largest modification of the GaAs host band is found over 2–4 eV BE. The energy separation from the top of the GaAs-host states to $E_F$ is in the order of 50 meV, after taking into account the experimental energy resolution, convolution with the Fermi function, and possible recoil effects [22]. We note that in a real impurity system, i.e., when disorder is included, Bloch states are never formed and the concept of delocalized states in the Mn-derived band with a clear $E$ vs $k$ relation cannot be fully defined. Thus the term “band” does not imply electronic states of well-defined crystal momentum, while the DOS remains a well-defined quantity. In the present case, angle-integrated HAXPES measures only the DOS: because of the high photon energy used ($h\nu \approx 5$ keV), band structure effects can be neglected [21].
In conclusion, the present experimental observations of a persistent diluted character of Mn in GaAs, together with $E_F$ located well above the GaAs valence band top, as found by Ohya et al. [8], suggest that the existence of a Mn-derived band which is not detached from the GaAs bands, could be compatible at the same time with localization (impurity band) character.

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