IOP Publishing New J. Phys. 19 (2017) 023006 https://doi.org/10.1088/1367-2630/aa5a42

New Journal of Physics
The open access journal at the forefront of physics

Deutsche Physikalische Gesellschaft DPG
IOP Institute of Physics
Published in partnership with: Deutsche Physikalische Gesellschaft and the Institute of Physics

RECEIVED
15 July 2016

REVISED
28 December 2016

ACCEPTED FOR PUBLICATION
18 January 2017

PUBLISHED
2 February 2017

**PAPER**

# Electronic structure of (Ga,Mn)As revisited

J Kanski[1], L Ilver[1], K Karlsson[2], I Ulfat[3], M Leandersson[4], J Sadowski[4,5] and I Di Marco[6]

[1] Department of Applied Physics, Chalmers University of Technology, SE-41296 Göteborg, Sweden
[2] Department of Engineering Sciences, University of Skövde, SE-54128 Skövde, Sweden
[3] Department of Physics, University of Karachi, Karachi 75270, Pakistan
[4] MAX IV Laboratory, Lund University, SE-221 00 Lund, Sweden
[5] Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, PL-02-668 Warszawa, Poland
[6] Department of Physics and Astronomy, Uppsala University, Box 516, SE-75120, Uppsala, Sweden

**E-mail:** janusz.kanski@chalmers.se

**Keywords:** dilute magnetic semiconductors, band structure, magnetic coupling

Supplementary material for this article is available online

## Abstract

The detailed nature of electronic states mediating ferromagnetic coupling in dilute magnetic semiconductors, specifically (Ga,Mn)As, has been an issue of long debate. Two confronting models have been discussed emphasizing host band versus impurity band carriers. Using angle resolved photoemission we show that the electronic structure of the (Ga,Mn)As system is significantly modified from that of GaAs throughout the valence band. Close to the Fermi energy, the presence of Mn induces a strong mixing of the bulk bands of GaAs, which results in the appearance of a highly dispersive band in the gap region of GaAs. For Mn concentrations above 1% the band reaches the Fermi level, and can thus host the delocalized holes needed for ferromagnetic coupling. Overall, our data provide a firm evidence of delocalized carriers belonging to the modified host valence band.

## Introduction

Although more than 20 years have passed since the first synthetization of a III–V-based dilute magnetic semiconductor [1], implementation of these materials in everyday spin-based electronics is as elusive as ever because the ferromagnetic transition temperature is much lower than desired. Rather remarkably, the physical origin of the ferromagnetic state is still debated, even for the prototype dilute magnetic semiconductor (Ga,Mn) As. A wealth of experimental data suggests that the magnetic coupling is mediated by spin-polarized holes, but the actual character of these holes has become an issue of fierce debate. Two main scenarios are discussed: acceptor induced holes in the host valence band versus holes in a more or less detached impurity band. Experimental evidence for the existence of an impurity band based on optical properties has been presented [2], though later studies suggested that these data are also consistent with the host valence band model [3]. Support for an impurity band scenario is also obtained from resonant tunneling experiments on quantum well structures [4] and from channeling in combination with magnetization, transport, and magneto-optical experiments [5]. In this last work the location of the Fermi level within the impurity band is emphasized to play a crucial role in determining the Curie temperature ($T_C$). Studies based on photoemission, instead, point to the coexistence of coupling mechanisms in the impurity band and host valence band models [6, 7]. The role of delocalized Mn-derived states near the top of the valence band has been emphasized in photoemission studies using very high photon energies [8], and the presence of delocalized Mn d-states has been inferred from observation of screening effects in core level spectra correlated with magnetic properties [9]. Here we do not detect any direct contribution from Mn 3d states, but find a strong modification of the host valence band. In a very recent photoemission study [10] it was found that the electronic structure of (Ga,Mn)As is heavily perturbed by disorder in the region of valence band maximum (VBM) relative to that of GaAs. However, these experiments were carried out only with radiation from a He discharge lamp and did not capture any of the main observations of the present angle resolved photoemission study, which instead uses synchrotron radiation. Furthermore, our sample design (see below) allowed us to make a more detailed and critical comparison between the electronic structures of pure GaAs and (Ga,Mn)As.

## Experimental aspects

While photoemission is the most direct probe of electronic states, its applicability is hampered by its intrinsic surface sensitivity: well-defined, atomically clean samples are required. This is not an issue in situations where the surface can be prepared by e.g. ion etching and annealing, but in the present case such treatment is prohibited because (Ga,Mn)As undergoes phase separation at temperatures above 300 °C. Indeed, in an earlier study [11] it was demonstrated that the electronic structure is modified by annealing, the most obvious effect being a shift of the Mn 3d binding energy from around 3.2 eV (for as-grown material) [7] to 4.3 eV (after post-growth treatment) [12]. Interestingly (and surprisingly), the latter value is still quoted in literature (see e.g. [13]), which further adds to a confusing discussion. Even if phase separation can be avoided by annealing at lower temperature [14], etching of a ternary system like (Ga,Mn)As may modify the surface composition and morphology in an uncontrolled way. An alternative is to use As capping to protect the surface against contamination during transfer between the growth and analysis units [15]. This again is a very delicate method, since the capping must be sufficiently thick to serve its purpose (typically 400 nm, see [16]). The As capping applied in [15] was only 0.5–1 nm thick, and the XAS reported in [15] did indeed show the structures characteristic for an oxidized sample [17]. On the other hand, a sufficiently thick As capping would have to be removed by heating, in which case an additional complication is unavoidable: during post-growth annealing interstitial Mn will diffuse to the surface and react with As to form MnAs overlayer/particles [18]. A different approach to avoid problems with the surface is to reduce the surface sensitivity of the photoemission spectroscopy by using a sufficiently high photon energy [6]. As will be shown here, features of major interest are confined near the center of the Brillouin zone, and would appear in an angular range of less than 0.5° from the surface normal at the photon energy used in [6]. Such features would not be resolved under experimental conditions like those in [6].

The only safe way to avoid complications with surface preparation is transfer of samples between the growth and analysis systems in ultrahigh vacuum (UHV). This is the strategy adopted in the present work, and was also followed in another very recent study [10]. Apart from this last work, the fact that the results presented here have not been found in any of the earlier studies shows unequivocally that sample handling is a decisive issue not only for magnetism [19] but also for the details of the electronic structure. The present data allow us to identify a connection between the magnetic and electronic properties of (Ga,Mn)As.

## Results and discussion

Two sets of experimental data are presented here, one obtained at MAX IV laboratory beamline I3, where a photoelectron spectrometer is connected to an MBE system, the other at the Swiss Light Source (SLS) ADRESS beamline. In the latter case the samples were transported in a UHV suitcase from the MBE system at MAX-lab. The (Ga,Mn)As layers were grown on n-type GaAs(100) substrates and the Mn concentration was determined using RHEED oscillations with an accuracy better than 0.1% [20]. To allow detailed comparison of spectra from GaAs and (Ga,Mn)As a mask was used during the growth, leaving a part of the substrate with clean GaAs. In this way spectra from the two materials could be recorded under identical conditions. The SLS data discussed here were recorded with the sample at around 200 K, while the MAX data were obtained at room temperature. In both cases the temperatures were far above the Curie temperature of as-grown samples, which is typically below 50 K. All samples with Mn concentrations above 0.5% showed $(1 \times 2)$ LEED patterns, while for pure GaAs the LEED pattern was $c(4 \times 4)$ (figure S1).

Figures 1(a) and (b) show photoemission intensity distributions obtained at SLS with circularly polarized 453 eV photons. On the whole, the data from GaAs and (Ga,Mn)As are similar except in the vicinity of VBM—for GaAs all bands (HH, LH, and SO) are observed up to VBM, while for (Ga,Mn)As the top parts of the bands are hardly distinguished. This region will be discussed further using the MAX-lab data, which were recorded with much better angular resolution and better statistics. There are other, less obvious differences, that are disclosed via intensity profiles. In figure 1(c) a pair of profiles is displayed, selected such that the in-plane momentum separations ($\Delta k_{//}$) between the light hole (LH) branches is the same (at the dashed lines in figures 1(a) and (b)). We find that $\Delta k_{//}$ between corresponding spin–orbit (SO) branches is somewhat larger for (Ga,Mn)As than for GaAs. In figure 2 we show how this difference in $\Delta k_{//}$ develops along the bands in the binding energy range 1.5–4.0 eV. A corresponding plot of $\Delta k_{//}$ between heavy and light hole bands does not reveal any significant difference between the two materials (figure S3). Clearly, the bulk band structure of GaAs is modified in a non-trivial way by the introduction of Mn, i.e. more than a rigid shift due to p-doping. Regarding

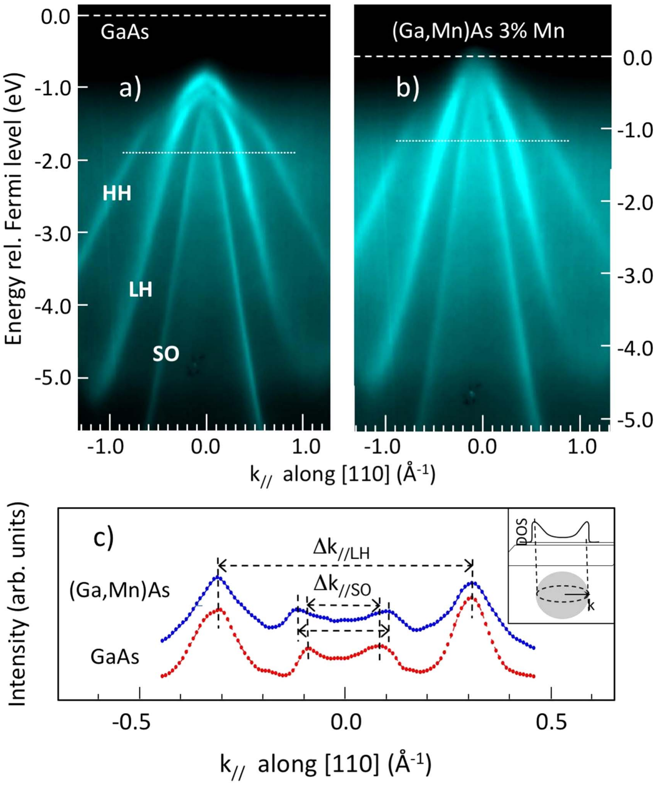

**Figure 1.** Photoemission intensity distributions from (a) GaAs(100)-c(4 × 4) and (b) (Ga,Mn)As(100)-(1 × 2) excited with circularly polarized 453 eV photons. (c) Intensity profiles extracted at the energies marked by dotted lines in (a) and (b). The inset shows a schematic model of the projected density of states (DOS) for a free-electron like band.

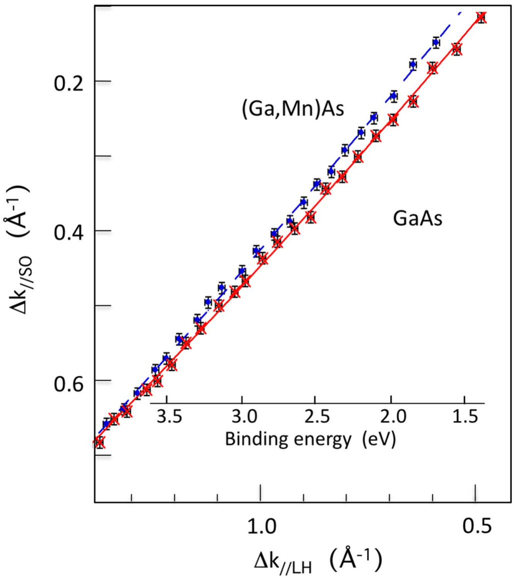

**Figure 2.** The $k_{//}$ separation between the two branches of the SO band as a function of the corresponding separation between the LH branches. The inserted binding energy scale refers to the GaAs data. The lines show parabolic fits to the respective data.

the origin of this modification, we note that early photoluminescence data from heavily Zn-doped GaAs showed a shift of the emission involving the SO band, that was ascribed to a smaller contribution to the spin–orbit energy in the dopant [21]. In analogy, it can be expected that the SO splitting should be reduced by replacing Ga with Mn in (Ga,Mn)As.

It is noted in figure 1 that the LH and SO bands are excited with approximately the same probability over a range of binding energies. This can be understood as an effect of final state lifetime broadening. The intensity

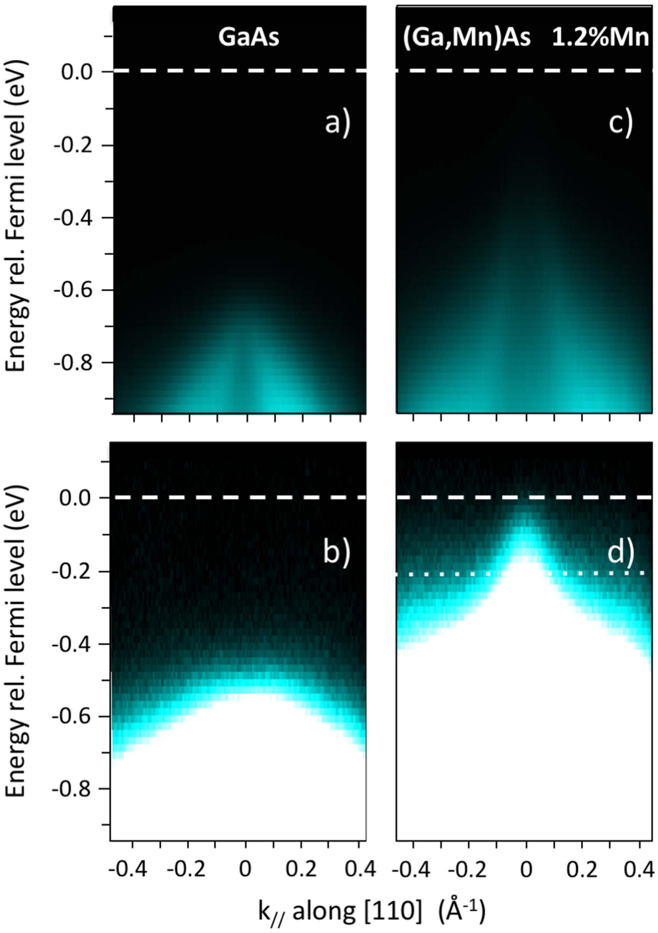

**Figure 3.** Photoemission intensity distributions the VBM region of (a) GaAs and (b) (Ga,Mn)As, excited with p-polarized 21 eV photons. (c) and (d) The same data as (a) but with a reduced threshold level. The dashed line indicates the Fermi energy and the dotted line in (d) represents the valence band maximum of GaAs as described in the text.

distribution then reflects the projected density of states. As illustrated schematically in the inset in figure 1(c), the projection of a spherical momentum distribution (i.e. $E \sim |\mathbf{k}|^2$) is a circle with maximum density of states at its periphery, and the intensity profile takes the experimentally observed 'suspension bridge' shape.

We now turn to the MAX-lab results. As for the SLS data, the valence band region is characterized by overall similarities between (Ga,Mn)As and GaAs and the SO band of (Ga,Mn)As is shifted up in energy (figure S2). A deformation of the SO band was also reported in an early photoemission study of (Ga,Mn)As [14], though the shift was in the opposite direction to that found here. The cause for this discrepancy is not clear, but the energy alignment is an obvious issue of concern—as described below, we have chosen to align the $X_3$ critical points, while in [14] (and likewise in [6]) the Fermi energy was used as a reference. The latter is obviously misleading because the doping situations in the two materials are very different. In figure 3 we show intensity distributions in the VBM region. As expected, the Fermi level in GaAs is pinned near midgap and as seen in figure 3(b), where the same data is displayed but on an 'overexposed' intensity scale the gap region is completely free from photoelectrons. For (Ga,Mn)As the emission extends towards higher energies (figure 3(c)), and when displayed on the same overexposed intensity scale (figure 3(d)), we see that it is distinctly peaked at the center. In figure 3(d) we have also indicated the VBM position of GaAs (dotted line), shifted in energy to take into account the different pinning situations. This energy was estimated using literature data [22, 23], according to which the separation between the $X_3$ point and VBM is in the range 6.7–6.9 eV. The dotted line marks the highest possible position based on these data, so it can be safely concluded that the narrow peak extends into the band gap region of GaAs. It is motivated to emphasize that one reason why this feature has eluded detection in previous studies (apart from the sample preparation issue discussed above) is its low intensity and angular confinement: in regular energy distribution curves the structure appears as a weak shoulder on a tailing background, and in experiments with limited angular resolution the dispersive character will be hardly discernible. Instead a slightly increased intensity will manifest itself as a peak in difference spectra [6, 15].

More detailed information specific of the feature underlying the narrow peak in figure 3(d) can be extracted by optimizing the saturation and threshold levels. In figure 4 we show such intensity distributions for samples

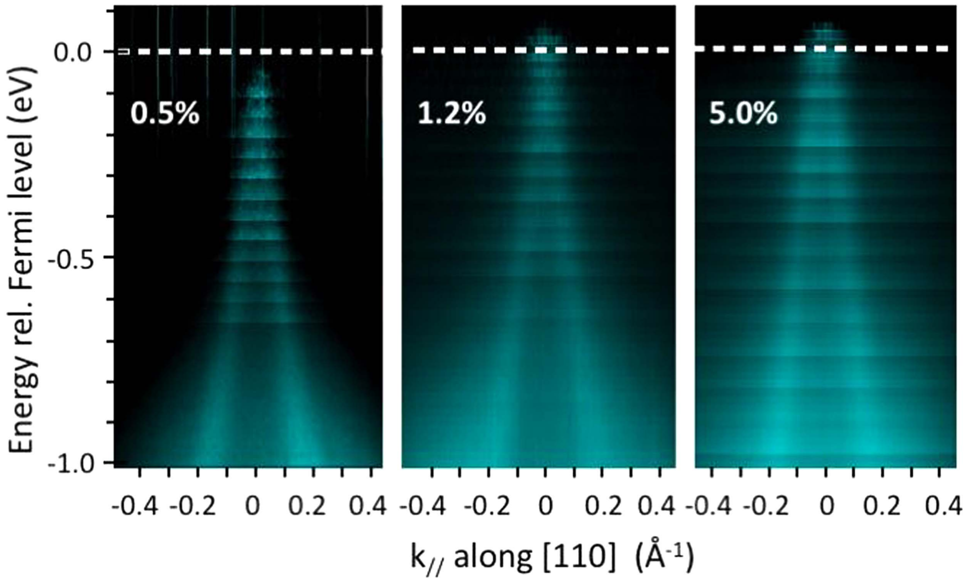

**Figure 4.** VBM data at room temperature from (Ga,Mn)As samples with (a) 0.5% (excited with 24 eV photons), (b) 1.2% and (c) 5% Mn (both excited with 25 eV photons). To emphasize the dispersing band, the data were sliced in energy and the threshold levels were gradually optimized. The dashed line indicates the Fermi level. The Curie temperature for the sample with 1.2% Mn was around 10 and 55 K for the 5.5% sample. No ferromagnetism was found for the sample with 0.5% Mn.

with three different Mn concentrations. Each distribution is composed from slices arbitrarily adjusted with respect to contrast. The set of data in figure 4 reveals an important connection between electronic and magnetic properties: for the 0.5% Mn sample, which does not show any ferromagnetism, the band does not reach the Fermi level. With 5% Mn the band appears broader, which can be understood as an upwards shift in energy. As a result, the density of states at the Fermi level is increased, and indeed the recorded $T_C$ for this sample was found to be around 50 K. The 1.2% sample is a borderline case with a measured $T_C$ of around 10 K.

The concentration dependence of the Mn-induced band is obviously matching the known magnetic properties [25]. The band reaching the Fermi level is an obvious candidate for hosting the delocalized holes needed for ferromagnetic coupling. Applying a simple free electron model, however, it is clear that the Fermi wave vector for this band is much too small to account for the density of carriers that are known to be present in ferromagnetic (Ga,Mn)As [26]. We must conclude that there is a large density of states not seen in our data. In this respect our results are in agreement with those reported in [10], where the intensity from top of the HH and LH bands in (Ga,Mn)As was found to be totally suppressed. Two questions need then to be addressed: (a) what is the reason for the apparent suppression of these bands, and (b) where are these states located. Since the states are not observed, the second question can only be discussed speculatively. Noting that ferromagnetism appears when the Fermi level enters the rapidly dispersing band, it is natural to assume that the HH/LH band maxima more or less coincide with the top of this band. The reason why the HH/LH bands are not directly observed is also unclear. It cannot be due to symmetry selection rules, as suggested in [10], because the states are observed in the corresponding data from GaAs (see figures 1 and 3). Instead we tentatively ascribe the fuzzy appearance of the VBM region in (Ga,Mn)As to hybridization of Mn derived states with the host valence band due to a combination of configuration mixing [17] and crystal field splitting the Mn states are expected to be spread out in energy and momentum coordinates. Moreover, their relatively small cross sections helps explaining why the mixed states with the HH/LH bands are not visible around the Fermi energy.

Having established the existence of a dopant-induced energy band above VBM, we proceed to examine its properties. Of immediate concern is the possibility that it may reflect a surface state. Within the photon energy range 20–35 eV, where the band is observed, we found no significant dependence of momentum along the surface normal. While this is normally a reliable signature of a surface state, several other observations contradict such interpretation. First, the band is not confined to the band gap region, but can be followed well below VBM. Second, no asymmetry was observed that could be connected with the surface reconstruction (as is the case for e.g. the GaAs(100)-2 × 4 surface [24]). Third, a well-defined and rapidly dispersing surface state band would require a well-ordered surface with long-range coherence. However, several studies (figure S1, [27]) have shown that the (1 × 2) reconstructed surface is characterized by disorder. Fourth, the band has been found quite stable against surface contamination (adsorption of residual CO and $N_2$) and is clearly observed even when the most prominent bulk derived features are strongly attenuated. All this leads us to conclude that the Mn-induced band is not a surface state but a feature of the bulk electronic structure. It is appropriate at this point to note that also in the above-mentioned angle-resolved photoemission study [14] a structure lacking dispersion along the surface normal was reported. In contrast to the Mn-induced band discussed here, however, that structure was located well below the Fermi level (0.5–1.0 eV), and did not show any in-plane dispersion. We tentatively ascribe the difference relative the present results to the ion etching treatment during surface preparation [14].

Features in the VBM region resembling those found here have been reported in a couple of theoretical studies [28, 29]. In these works an excursion of a host-derived majority spin band is predicted above VBM. However, these studies address (Ga,Mn)As in its ferromagnetic state, while the data discussed here were recorded well above $T_C$. Using the ferromagnetic phase to understand the paramagnetic phase of (Ga,Mn)As is fully justified only if their electronic structures are qualitatively similar. We note that electronic structure calculations of the paramagnetic state in the disordered local moments (DLM) picture give substantially the same magnetic local moment and (spin-integrated) spectral properties of the ferromagnetic phase [30]. Although the DLM picture involves only an approximate treatment of spin-fluctuations, the absence of drastic changes in the electronic structure across the ordering temperature is not uncommon for systems where the magnetic moments arise from strongly localized electrons [31]. The localized nature of the Mn-3d states in (Ga,Mn)As is indeed widely accepted [18], and is also suggested by the multiplet-like spectrum reported recently [7].

We return now to the question concerning the excitation of the Mn-induced band. In 'regular' crystal momentum assisted photoemission, dispersive bulk states are observed at a fixed in-plane momentum and appear at different binding energies in spectra excited with different photon energies. Reversibly, the lack of such photon energy dependence is a typical property of a surface state. As already discussed, various observations contradict a surface state interpretation in the present case. A striking observation is the very low spectral intensity, about two orders of magnitude smaller than that of the surface state of the GaAs surface. Since we associate the band with Mn impurities, it is natural to suspect that the low intensity may be directly related to the low density of impurity atoms. However, apart from the fact that we do not observe any clear proportionality between the intensity and Mn concentration over a range of 1%–5%, this would not explain the lack of dispersion along the surface normal. Alternatively, the low intensity can be taken as an indication of a basically different excitation mechanism from that in regular photoemission. A mechanism that is usually ignored in the analysis of photoemission spectra is the one based on the change of the photon field in the surface region, so called surface photoemission. Surface photoemission has been discussed extensively in the past [32], mainly in connection with excitation of sp-bands in metals. By this mechanism the momentum selectivity along surface normal is relaxed while the in-plane momentum is preserved. The emission should then reflect the projected density of states, as discussed in connection with the SLS data, and the intensity distribution should appear as a dispersing band just as the SO band in figure 1. If this is correct, corresponding emission should also be found for GaAs. To test this hypothesis we report intensity distributions from the VBM region of pure GaAs (figure 5(a)) and (Ga,Mn)As with only 0.4% Mn (figure 5(b)). The data are displayed in the 2nd derivative mode with high intensity represented by bright color. For GaAs we have indicated the bulk bands using effective masses and SO splitting from literature [33]. A feature of particular interest in figure 5(a) is the bright spot at normal emission around 1.3 eV binding energy. This spot marks the top of a triangular field, which can be followed about 1 eV down in energy. As suggested by the dashed lines, we associate the bright spot with the top of the SO band. One can also discern a bright path coinciding with the downward dispersing SO band. The shaded triangular field, reflecting a relatively high intensity, is contained within the SO band in much the same way as the field between the SO branches in figure 1. We can conclude that the intensity distribution can be explained as projected density of states, supporting the above interpretation of the excitation mechanism. For (Ga,Mn)As the intensity distribution contains a similar triangular bright region, figure 5(b), but the spot marking the top of the triangle is missing and the triangular region appears to extend through the VBM into the band gap of GaAs. The data show that the band structure of (Ga,Mn)As cannot be considered as p-doped GaAs, but rather as a system in which the energy bands of the host material are intermixed and modified by the Mn impurities. A more detailed description of the band structure of (Ga,Mn)As requires a theoretical analysis that takes into account the impurities as well as the interaction with the hole gas.

While the connection between the magnetic properties and the dispersive Mn-induced band is indeed suggestive, the actual origin of the Mn-induced modifications remains to be clarified. From a theoretical point of view, in addition to the doping induced shift, changes in the electronic structure are due to the hybridization with impurity states and disorder. Moreover, an effect that is generally overlooked in the literature on dilute magnetic semiconductors is the interaction between host electrons and the hole gas. A well-known consequence of such interaction is a dopant-induced bandgap narrowing [34–36]. Recalling that $\mathrm{Mn_{Ga}}$ is an acceptor in GaAs, the hole density in samples with Mn concentration in the range of 1% is above $10^{20}$ $\mathrm{cm}^{-3}$ (even taking into account compensation due to Mn interstitials). With such strong doping the band gap narrowing is expected to be in the region of 100 meV. It is conceivable, therefore, that the present observations are, at least partly, due to the effects of the dopant-induced hole gas.

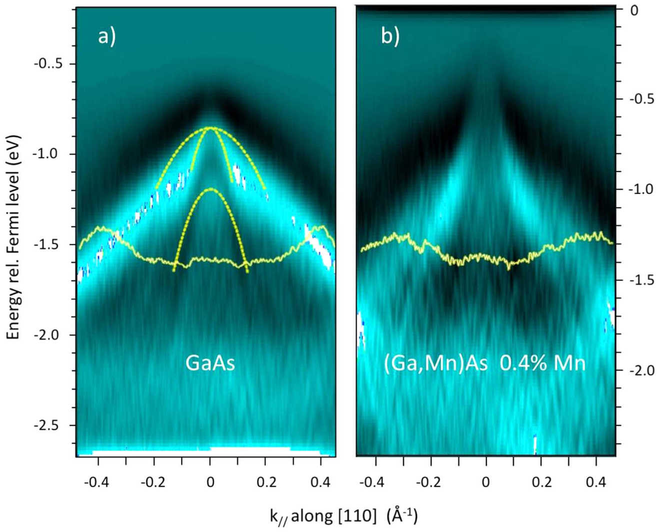

**Figure 5.** VBM data at room temperature from (a) GaAs and (b) (Ga,Mn)As with 0.4% Mn, excited with 25 eV photon energy. The two figures are aligned at the $X_3$ density of states peaks. Intensity profiles are indicated in both cases at 1.5 eV binding energy. For GaAs we have indicated the bulk bands using effective masses and SO splitting from [32].

## Summary

In conclusion, the present study provides two new observations with impact on the view on the electronic states in (Ga,Mn)As: (a) we show that the band structure of the host material is changed in a non-trivial way, such that the bulk bands are modified over a wide energy range. In [8] the largest Mn derived modification of the GaAs band structure was actually predicted in the binding energy region 2–4 eV, though this was not verified experimentally; (b) most importantly, a highly dispersive Mn-induced energy band is found *above* the VBM of the host material. The development of this band can be observed at Mn concentrations below 0.5%. For concentrations above 1% this band reaches the Fermi level (that is located in the band gap of GaAs) and can host holes mediating the ferromagnetism. However, although the appearance of holes in this band correlates well with the magnetic properties of (Ga,Mn)As, the density of states in this band is too small to accommodate the high density of carriers known to be present from other experiments. It is concluded that additional states, not observed in photoemission, are present in the gap region of GaAs and that holes in these states are formed more or less parallel with holes in the highly dispersive band.

Apart from these novel observations, our data are in good agreement with the most recent photoemission measurement what regards the gross features, e.g. the binding energy of the main Mn 3d peak at around 3 eV [10, 15]. Nevertheless, while we find that the Fermi level is in the gap region of GaAs, in [10] it is concluded to be deep below VBM crossing the LH/HH bands. In comparison with other recent studies, in which modifications of the host valence band have been inferred (e.g. [8]), it is important to stress that the present data provide a qualitatively different picture: the modifications are not described as Mn-*derived* but Mn-*induced*. The distinction might appear subtle, but it is indeed significant. In the former case the modification is due to intermixing of Mn 3d states with host valence states, the Mn states retaining their Gaussian line shape, in the latter the Mn impurities induce changes in the host band structure. The present finding is of crucial importance, since it reconciles the successes obtained by the p-d Vonsovsky-Zener model of magnetism [19] with spectroscopic data favouring the valence band model. Our study also reveals that the host valence band is modified by Mn-impurities such that the effect of the dopants is not just a shift of the chemical potential. Furthermore, no evidence of a detached impurity band is found even for concentrations below 0.5%, which suggests that the host valence band model (delocalized holes) stays more or less valid till the Anderson metal-to-insulator transition.

## Acknowledgments

Valuable discussions with Olle Eriksson, Barbara Brena and Olle Gunnarsson are gratefully acknowledged. We also wish to thank Vladimir Strocov and Federico Bisti for important experimental assistance at SLS and Roland Mathieu for the magnetic characterization of our samples. JK and LI wish to express gratitude to Peter Apell for all support. JS acknowledges partial support from the research project No: 2014/13/B/ST3/04489 financed through the National Science Centre (Poland).

## Q1 References

[1] Munekata H, Ohno H, von Molnar S, Segmüller A, Chang L L and Esaki L 1989 *Phys. Rev. Lett.* **63** 1849–52
[2] Burch K S, Shrekenhamer D B, Singley E J, Stephens J, Sheu B L, Kawakami R K, Shiffer P, Samarth N, Awschalom D D and Basov D N 2006 *Phys. Rev. Lett.* **97** 087208
[3] Jungwirth T *et al* 2010 *Phys. Rev. Lett.* **105** 227201
[4] Ohya S, Takata K and Tanaka M 2011 *Nat. Phys.* **7** 342–7
[5] Dobrowolska M, Tivakornsasithorn K, Liu X, Furdyna J K, Berci M, Yu K M and Walukiewicz W 2012 *Nat. Mater.* **11** 444–9
[6] Gray A X *et al* 2012 *Nat. Mater.* **11** 957–62
[7] Di Marco I, Thunström P, Katsnelson M I, Sadowski J, Karlsson K, Lebègue S, Kanski J and Eriksson O 2013 *Nat. Commun.* **4** 2645
[8] Fujii J *et al* 2013 *Phys. Rev. Lett.* **111** 097201
[9] Fujii J *et al* 2011 *Phys. Rev. Lett.* **107** 187203
[10] Souma S, Chen L, Oszwaldowski R, Sato T, Matsukura F, Dietl T, Ohno H and Takahashi T 2016 *Sci. Rep.* **6** 27266
[11] Adell M, Ilver L, Kanski J, Sadowski J, Mathieu R and Stanciu V 2004 *Phys. Rev.* B **70** 125204
[12] Rader O *et al* 2004 *Phys. Rev.* B **69** 075202
[13] Szwacki N G, Majewski J A and Dietl T 2015 *Phys. Rev.* B **91** 184409
[14] Okabayashi J, Kimura A, Rader O, Mizokawa T, Fujimori A, Hayashi T and Tanaka M 2001 *Phys. Rev.* B **64** 125304
[15] Kobayashi M *et al* 2014 *Phys. Rev.* B **89** 205204
[16] Kawai N J, Nakagawa T, Kojima T, Ohta K and Kawashima M 1984 *Electron. Lett.* **20** 47–8
[17] Edmonds K, Farley N R S, Campion R P, Foxon C T, Gallagher B L, Johal T K, van der Laan G, MacKenzie M, Chapman J N and Arenholz E 2004 *Appl. Phys. Lett.* **84** 4065–7
[18] Sadowski J *et al* 2005 *Appl. Phys. Lett.* **87** 263114
[19] see e.g. Dietl T and Ohno H 2014 *Rev. Mod. Phys.* **86** 187–251
[20] Sadowski J, Domagala J Z, Bak-Misiuk J, Kolesnik S, Sawicki M, Swiatek K, Kanski J, Ilver L and Ström V 2000 *J. Vac. Sci. Technol.* B **18** 1697–700
[21] Olego D and Cardona M 1980 *Phys. Rev.* B **22** 886–93
Cardona M 1969 *Modulation Spectroscopy* ed F Seitz *et al* (New York: Academic) pp 65–73
[22] Chiang T-C, Ludeke R, Aono A, Landgren G, Himpsel F J and Eastman D E 1983 *Phys. Rev.* B **27** 4770–8
[23] Williams G P, Cerrina F, Lapeyre G J, Anderson J R, Smith R J and Hermanson J 1986 *Phys. Rev.* B **34** 5548–57
[24] Larsen P K, van der Veen J F, Mazur A, Pollmann J, Neave J H and Joyce B A 1982 *Phys. Rev.* B **26** 3222–37
[25] see e.g Dietl T and Ohno H 2006 *Mater. Today* **9** 18–26
[26] Seong M J, Chun S H, Cheong H M, Samarth N and Mascarenhas A 2002 *Phys. Rev.* B **66** 033202
[27] Othake A, Hagiwara A and Nakamura J 2013 *Phys. Rev.* B **87** 165301
[28] Sato K *et al* 2010 *Rev. Mod. Phys.* **82** 1633–90
[29] Ernst A, Sandratskii L M, Bouhassoune M, Henk J and Lüders M 2005 *Phys. Rev. Lett.* **95** 237207
[30] Bergqvist L, Eriksson O, Kudrnovský J, Drchal V, Bergman A, Nordström L and Turek I 2005 *Phys. Rev.* B **72** 195210
[31] Tjernberg O, Söderholm S, Chiaia G, Girard R, Karlsson U O, Nylén H and Lindau I 1996 *Phys. Rev.* B **54** 10245–8
[32] see e.g. Levinson H J, Plummer E W and Feibelman P J 1979 *Phys. Rev. Lett.* **43** 952–5
Hansen E D, Miller T and Chiang T-C 1997 *Phys. Rev.* B **55** 1871–5
[33] http://ioffe.ru/SVA/NSM/Semicond/GaAs/bandstr.html
[34] Abram R A, Rees G J and Wilson B L H 1978 *Adv. Phys.* **27** 799–892
[35] Sernelius B E 1987 *Phys. Rev.* B **36** 4878–87
[36] Persson C, Ahuja C R and Johansson B 2001 *Phys. Rev.* B **64** 033201