Resonant photoemission of Ga$_{1-x}$Mn$_x$As at the Mn $L$ edge

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DOI: 10.1103/PhysRevB.69.075202 PACS number(s): 75.50.Pp, 79.60.Bm, 71.27.+a

I. INTRODUCTION

In the research field of diluted magnetic semiconductors, the recent observation of long-range ferromagnetic order represented a major breakthrough. The materials that exhibit this ferromagnetic behavior are the Mn-doped III-V compounds InAs and GaAs prepared by molecular-beam epitaxy. In these materials, Mn occupies Ga or In sites of the zinc blende lattice. It is understood that the origin of ferromagnetism is connected to a twofold effect of the Mn impurities: on the one hand they provide localized magnetic moments, on the other hand they act as a hole dopant. Nevertheless, the physics of the long-range ferromagnetic interaction remains controversial, basic questions being whether this interaction is mediated by Mn 3$d$–Mn 3$d$ interaction or Mn 3$d$–As 4$p$ and whether the latter would couple spins parallel or antiparallel. More precise knowledge of the electronic structure of the Mn impurities in this system is therefore required.

Previously, we studied the Mn 2$\rho$ core level by x-ray photoelectron spectroscopy and analyzed the spectrum with its strong satellite using configuration-interaction calculations taking into consideration the local surrounding of the Mn impurity in a cluster model. The Mn 4$d$ electron number was determined to be $\approx 5$ and both Mn$^{1+2}$ and Mn$^{3+}$ states were found to be in agreement with the experimental data. The exchange constant $N\beta$ was determined as $-1.2 \pm 0.2$ eV meaning antiferromagnetic Mn 3$d$–As 4$p$ interaction in the case of the half-occupied Mn$^{2+}$ ion. Because of the strong magnetic coupling between Mn$^{3+}$ and an As 4$p$ hole, the hole will be responsible for the long-range magnetic interaction. Valence-band photoemission at and above the Mn M edge (50 eV) permitted assignment of structures in the local Mn 3$d$ contribution to the excitation spectrum to $d^3$, $d^2L_\infty$, and $d^0L^2$ configurations, i.e., configurations where the number of electrons transferred from As 4$p$ orbitals to Mn 3$d$ is zero, one, and two, respectively. Besides a strong main peak around $-4.5$ eV assigned to $d^2L_\infty$, an intense valence-band satellite was seen to be caused by $d^3$ plus $d^0L^2$ contributions. The average Mn configuration was determined to be $3d^{5.3 \pm 0.1}$.
The possibility to distinguish Mn 3d derived states by resonant photoemission at the Mn $L$ edge is particularly important for the region near the Fermi energy. Apart from intensity predicted for $d^5L$ near $-2$ eV, there is almost no intensity near $E_F$ in the spectra measured. Substantial Mn 3d derived intensity at $E_F$ had been predicted by coherent-potential approximation local-density calculations for In$_{1-x}$Mn$_x$As and Ga$_{1-x}$Mn$_x$As in Ref. 7 with the interesting consequence that these systems would belong to the class of half metals. Angle-resolved photoemission of Ga$_{1-x}$Mn$_x$As(100), $x = 0.069$, showed very similar band dispersions along $\Gamma$-X as in pure GaAs(100), however, shifted by 100–200 meV for large portions of the $\Delta_1$ band. More importantly, the experiments permitted the direct observation of the acceptor states induced by Mn doping near $E_F$ by comparison to pure GaAs spectra for various photon energies also without resonant excitation.$^8$

Recently, photoemission spectra have been studied in dependence of the Mn concentration.$^9$ Reference 9 obtains a concentration-dependent position of the Mn 3d emission from Ga$_{1-x}$Mn$_x$As with $\sim -3.5$ eV for $x = 0.045$ and 0.055. Other spectral features are not reported. In particular, no satellite emission was seen, and it was concluded that local-density theory gives a proper description of the Mn contribution to the spectra.$^9$

Magnetic circular x-ray dichroism (MCXD) in absorption at the Mn $L$ edge for Ga$_{1-x}$Mn$_x$As has been reported$^{10,11}$ and analyzed in comparison to theory.$^{11,12}$ For the number of Mn 3d electrons, 5.08 has been obtained$^1c$ and a small fraction of ferromagnetically ordered Mn moments among all Mn impurities.

As at the $M$ edge, resonant photoemission at the $L$ edge can be described as interference between a direct photoemission channel $2p^63d^{n}\rightarrow 2p^63d^{n-1}+e^-$ and the decay of an excited state $2p^53d^{n+1}-2p^53d^{n-1}+e^-$. Resonant photoemission at the transition-metal $L$ edge has been predicted to lead to an enhancement of valence-band photoemission much larger than that at the $M$ edge,$^{13}$ and experiments have been performed for compounds$^{14,15}$ and metals,$^{16}$ but despite its potential the method has not yet been applied to diluted systems, to our knowledge. For the size of the enhancement, values between 10 and 100 have been quoted.$^{14}$ It is expected that dilution increases electron correlation and that an enhanced electron correlation will increase the resonant enhancement. Moreover, due to the dilution, we can determine the enhancement precisely via normalization to the core-level intensity of a host constituent. These advantages together with the large size of the enhancement permit a discussion of the 3d spectral shape rather independently from the spectrum of the host material. Due to the comparatively large probing depth at kinetic energies around the $2p$ binding energy ($\sim 10$ Å), the resulting 3d contribution is rather independent of the electronic structure of the surface and its quality. The Mn 3d contribution determined in this way will be compared to new calculations and to previous experimental results performed at higher surface sensitivity.

II. EXPERIMENTS

Samples were an n-type GaAs(100) crystal and a 50-nm-thick epitaxial film of Ga$_{1-x}$Mn$_x$As, $x = 0.043$, grown at 250°C on top of an Al$_{0.8}$Ga$_{0.2}$As buffer layer and subsequently capped with an As cap of $\approx 100$-nm thickness.$^{17}$ The sample had a Curie temperature of $\approx 60$ K. Decapping and removal of oxidized layers was done with noble-gas ion sputtering monitored by Mn 2$p$ photoemission as before.$^{5,18}$

In order to establish a $p(1 \times 1)$ low-energy electron-diffraction pattern while avoiding formation of NiAs-type MnAs precipitates, the sample was repeatedly annealed up to 240°C as maximum. The sample mounting ensured that the GaAs reference sample was heated to the same temperature.

Measurement temperature was 30 K. Synchrotron radiation from the UE56/2 PGhelical undulator beam line$^{19}$ was used to excite photoelectrons, namely, linearly polarized light of 62.5 eV and circularly polarized light around the Mn $L$ edge ($\sim 640$ eV). Photoemission spectra were measured with an Escalab MK2 spherical analyzer in normal-emission geometry at $1^\circ$ angle resolution and 50-meV energy resolution for 62.5-eV photon energy and with angle integration and 0.8-eV resolution for energies around the Mn $L$ edge. X-ray absorption spectra were measured with a total-yield channeltron during simultaneous scanning of monochromator and undulator. Base pressure was $2 \times 10^{-10}$ mbar.

For an overview, Fig. 1 shows resonant photoemission spectra for the Ga$_{1-x}$Mn$_x$As, $x = 0.043$, and pure GaAs as well as the difference spectra representing the Mn 3d contribution. The energy range includes the Ga 3p core levels and this was used for normalization. The spectra were superimposed precisely taking into account the Ga concentration (100% and 95.7%, respectively). The much stronger enhancement of the Mn 3d signal at the Mn $L$ edge (640.3 eV) as compared to a photon energy above the Mn $M$ edge (62.5 eV) is apparent from the figure. Figure 2 shows the photon-energy dependence more in detail. Photon energies are indicated with the x-ray absorption spectrum in the inset. Below the resonance [Fig. 2(b), 638.5 eV] the Mn 3d contribution is negligible whereas on resonance [Fig. 2(c), 640.3 eV] it is dominant. The main peak at $-4.3$ eV experiences a giant enhancement at the $L_3$ maximum by a factor of 20 with respect to the pre-edge spectrum (638.5 eV). Besides the main peak, there appears a satellite structure and intensity between the main peak and $E_F$. Although the satellite seemingly possesses a structure, most likely the dip around $-8.5$ eV is just intensity that has insufficiently been removed by the subtraction. In addition, the sample has been magnetized by a pulse along the in-plane [010] direction. A sizeable magnetic circular dichroism effect was not observed in the photoemission spectrum at 640.3-eV photon energy after reversing the helicity of the synchrotron radiation. This is in line with the small magnetic circular dichroism effect measured in x-ray absorption.$^{10,11}$ The x-ray absorption lineshape, however, is smoother and deviates more strongly from the atomic $d^5$ configuration than in Refs. 10 and 11.

Above the $L_3$ edge, the photoemission intensity is still enhanced, however, the spectral shape is dominated by emission around kinetic energies where LMM Auger contributions are expected. These are marked by an arrow in Fig. 2(d). This intensity can still be distinguished in the $L_2$-edge range [Figs. 2(e) and 2(f)].
to all 3d-transition-metal monoxides in Ref. 13 where a detailed description of the method can be found. In brief, the initial state considers three configurations of the MnAs$_4$ cluster, i.e.,

$$|i\rangle = \alpha_0|3d^5\rangle + \alpha_1|3d^6L\rangle + \alpha_2|3d^7L^2\rangle.$$  

Here, $L$ denotes a ligand hole, which corresponds to the transfer of an electron from an As 4$p$ orbital to a Mn $d$ orbital. The charge-transfer energy is defined as $\Delta = E(3d^6L) - E(3d^5)$ with $E(3d^6L)$ and $E(3d^5)$ being the average energies of the $3d^6L$ and $3d^5$ configurations, respectively. The $3d$-$3d$ Coulomb interaction energy is $U_{dd} = E(3d^6) + E(3d^4) - 2E(3d^5)$. The transfer integrals describing the hybridization between Mn 3$d$ and As 4$p$ are expressed in terms of Slater-Koster parameters $(pd\sigma)$ and $(pd\pi)$. As usual, the $2p$-$3d$ Coulomb interaction energy $U_{cd}$ has been tied to $U_{dd}$ by the assumption $U_{dd}/U_{cd} = 0.8$. The intermediate state is given by

$$|m\rangle = \beta_0|2p^53d^6\rangle + \beta_1|2p^53d^2L\rangle + \beta_2|2p^53d^3L^2\rangle,$$

and the final state of Mn 3$d$ photoemission is given by

$$|f\rangle = \gamma_0|3d^4\rangle + \gamma_1|3d^2L\rangle + \gamma_2|3d^3L^2\rangle.$$

The resonant photoemission spectrum for photon energy $\omega$ and photoelectron energy $\epsilon$ is expressed as

$$F(\omega, \epsilon) = \sum_i |\langle f|T(\omega)|i\rangle|^2 \delta(\omega + E_i - \epsilon - E_f)$$

with initial- and final-state energies $E_i$ and $E_f$, respectively, $\langle f|T(\omega)|i\rangle$ being the direct product of the final state $|f\rangle$ of the MnAs$_4$ cluster and the photoelectron final state $|\epsilon\rangle$. The $T$-matrix $T(\omega)$ includes perturbation operators for the direct dipole transition from 3$d$ to $e\ell_1$, for the dipole transition from 2$p$ to 3$d$, and for the Coster-Kronig decay processes from the intermediate state $|m\rangle$.

Figure 3 shows at the top the calculated x-ray absorption spectrum. Capital letters denote photon energies for which resonant photoemission spectra are displayed in the bottom panel. The parameters are the same as those used in Refs. 5 and 6, namely, $\Delta = 1.5$ eV, $(pd\sigma) = 1.0$ eV, and $U_{dd} = 3.5$ eV. The calculation reproduces the x-ray absorption spectrum of Fig. 2 very well apart from the splitting at the $L_2$ edge which has vanished as compared to previous work. Together with the multiplet lines we show photoemission spectra broadened by a Gaussian of 1.4-eV full width at half maximum. The off-resonant spectrum $A$ shows a strong main peak and strong satellite. Because of $\Delta < U_{dd}$, the main peak is assigned to $3d^5L$ and the satellite to $3d^4$ configurations. The on-resonance spectrum $C$ is strongly enhanced but otherwise quite closely resembles the off-resonance spectrum $A$. The spectral shape does change considerably in the $L_3$ region, $F$, and $G$. It appears as if the relative enhancement of the satellite region with respect to the main peak is rather driven by energy levels in an intermediate energy range (2-eV higher binding energy than the main peak) where mainly $3d^4$ and $3d^6L^2$ states contribute.
IV. DISCUSSION

Both experiment, Fig. 2, and theory, Fig. 3, indicate that photoemission spectra at the $L_3$ edge can very well be used to extract the Mn 3$d$ spectral weight. Both show that the enhancement is so large that the characteristic features can be appreciated even without the exact subtraction of the host-material spectrum as it was conducted here. We can also estimate from Figs. 2 and 3 that about half of the intensity tentatively assigned to incoherent Auger transitions in Fig. 2 is, by comparison to spectrum $E$ of the calculation, to extract the Mn 3$d$ spectral weight. Both show that the enhancement is so large that the characteristic features can be appreciated even without the exact subtraction of the host-material spectrum as it was conducted here. We can also estimate from Figs. 2 and 3 that about half of the intensity tentatively assigned to incoherent Auger transitions (arrows in Fig. 2) is.
has directly been measured from molybdenum clamps in contact with the sample). Instead, incoherent Auger contributions, the finite width of the host valence band, and electron-phonon interaction are possible sources of the strong broadening. Among these, electron-phonon interaction will be limited by the total width of 1.25 eV measured from the Ga 3d core levels displayed in Fig. 1. We believe that the width of the GaAs valence band is the main source of the broadening. For Cd$_{1-x}$Mn$_x$Te, the Andersen impurity model has been applied, and a Mn 3$d$ density of states has been obtained that is similar to the configuration-interaction cluster model but with broad spectral features.

Figure 4(b) compares the new data to the $M$-edge resonant photoemission of Ga$_{1-x}$Mn$_x$As, $x=0.069$ (Ref. 6). The spectra are very similar but the intensity of the satellite is higher when measured at 50-eV photon energy, and the higher intensity has very well been reproduced by the configuration-interaction calculation in Ref. 6 for a parameter set identical to the present one. This deviation was already noted for NiAs-type MnTe where the Mn 3$d$ satellite intensity is also weaker as compared to the main peak for $L$-edge than for $M$-edge resonant photoemission experiments.

Finally, we superimpose in Fig. 4(c) the 62.5-eV difference spectrum for the same Ga$_{1-x}$Mn$_x$As, $x=0.043$, sample. The difference spectrum at this photon energy is determined by enhanced Mn 3$d$ photoionization cross section instead of resonant Mn $M$-edge photoemission, and the photon energy is high enough to keep Auger transitions out of the energy range of interest. Obviously, at this energy the determination of the difference spectrum is more sensitive to GaAs subtraction than for resonant photoemission at the $L$ edge because the enhancement is smaller, band-structure effects are stronger, and surface effects can contribute more strongly. Details of the annealing procedure may therefore matter much more. Note that difference spectra at 70-eV photon energy have led to extra structure around $-2$ eV and even to negative intensities. This could be due to surface states as well as Mn-induced shifts of the bulk GaAs valence bands as established for the $\Delta_1$ band. These are reasonable causes since the difference between 50- and 48-eV photon-energy spectra from the same sample as studied at 70 eV is completely positive. The surface sensitivity (which is very similar at 50 and 70 eV) is, therefore, a matter of the GaAs host. Taking this into account, the fact that the present difference spectrum at 62.5 eV gives a rather good rendering of the Mn 3$d$ contribution indicates that choice of the photon energy indeed influences the results through the corresponding direct transitions of surface and bulk states of the GaAs host and that there is no indication for a particular surface dependence of the Mn 3$d$ contribution itself.

The 62.5-eV spectrum and the 640.3-eV spectrum agree with respect to their extremely weak intensity at $E_F$ [Fig. 4(c)]. Although the intensity of the 62.5-eV spectrum rises much steeper, the intensity becomes very weak at the same energy (about $-0.3$ eV). The low intensity at $E_F$ rules out a strong Mn 3$d$ contribution there. This means also that while Ga$_{1-x}$Mn$_x$As may be a half metal as suggested in Ref. 7, the half metallicity cannot result from Mn 3$d$ states as obtained.
in Ref. 7. Half metallicity may result instead from full polarization of As 4p states by interaction with Mn 3d. On the other hand, this result confirms the importance of As 4p holes as mediators of the magnetic coupling.

An expectation connected to resonant photoemission at the L edge is sensitivity to the electron configuration. Resonant photoemission at the L-edge of CuO (Ref. 14) is a particular example since the decay channel can principally enhance $3d^{10}$ through $3d^9 + h\nu \rightarrow 2p^6 3d^{10} - 2p^6 3d^8 + e^- \text{ but not } 3d^9 L$ final states since a corresponding channel does not exist. In the present case of Mn$^{2+}$, both $3d^5 + h\nu \rightarrow 2p^6 3d^6 \rightarrow 2p^6 3d^4 + e^-$ and $3d^9 L + h\nu \rightarrow 2p^6 3d^7 L \rightarrow 2p^6 3d^5 L + e^-$ exist and have similar matrix elements and transition probabilities. Therefore, on- and off-resonance spectra ($A-C$) are very similar to each other in Fig. 3.

We have to caution that our analysis based on the configuration-interaction scheme is limited by the assumption of identical Mn sites. Although the reason for the different x-ray absorption lineshape has not yet been established, MCXD data indicate that the ferromagnetically ordered portion of Mn atoms is small. Spin-resolved photoemission would give the 3d density of states of the ferromagnetically aligned Mn atoms. In resonant photoemission at the Mn M edge, the spin polarization was too small to extract a density of states. Mn L-edge resonant photoemission with its high intensity and small GaAs host signal is possibly better suited for spin-resolved studies.

Finally, we want to briefly return to the probing depth. It was recently argued that photoemission data obtained at photon energies in the vacuum-ultraviolet range cannot probe bulk properties and that energies in the soft-x-ray region need to be used. According to this view, the resonant valence-band photoemission at the L edge would probe bulk properties while the one at the M edge does not. Consequently, parameters deduced from the Mn 2p core level measured at $\approx 600$-eV kinetic energy represent the bulk whereas those from resonant valence-band photoemission at the Mn M edge and above it (kinetic energies between 45 eV and 65 eV) do not. The present study confirms the conclusions and the values of the parameters $\Delta$, $U_{dd}$, and $(p \sigma)$ from both previous studies and reassures that the reduced probing depth of resonant photoemission at the Mn M edge does not affect the conclusions. This is likely to be connected to the careful surface preparation exercised but is also due to the dilution. The applicability of the cluster model emphasizes the importance of nearest-neighbor atoms. As long as Mn remains on substitutional lattice sites and does not segregate to the topmost atomic layer, its electronic structure will remain largely the same. On the other hand, segregation of Ga or As would not affect our results very much as Mn atoms from deeper inside the bulk would still contribute to our difference spectra. In this case, the probing depth of the Mn 3d signal would even increase.

V. CONCLUSIONS

We studied resonant photoemission of $p(1 \times 1)$ Ga$_{1-x}$Mn$_x$As(100), $x = 0.043$, and $p(1 \times 1)$ GaAs(100) at photon energies above the Mn M edge and through the Mn L edge. The huge enhancement at the L edge ($\sim 20$) facilitates the extraction of the Mn 3d spectral contribution which is characterized by a three-peak structure including an intense correlation satellite. The x-ray absorption and resonant photoemission spectra are well described by a calculation using configuration interaction with multiplet splitting on a MnAs$_4$ cluster model. Experiment and model calculations agree with our previous work at the M-edge and are at variance with x-ray absorption and with recent photoemission results which obtained no satellite and suggested a description by an itinerant model.

ACKNOWLEDGMENT

This work was supported by BMBF under Contract No. 05 KS11PA/0 and by a Grant-in-Aid for Scientific Research in Priority Area “Semiconductor Spintronics” (Contract No. 14076209) from MEXT, Japan.

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