Photoemission and x-ray absorption studies of the isostructural to Fe-based superconductors diluted magnetic semiconductor Ba$_{1-x}$K$_x$(Zn$_{1-y}$Mn$_y$)$_2$As$_2$


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The electronic and magnetic properties of a new diluted magnetic semiconductor (DMS) Ba$_{1-x}$K$_x$(Zn$_{1-y}$Mn$_y$)$_2$As$_2$, which is isostructural to so-called 122-type Fe-based superconductors, are investigated by x-ray absorption spectroscopy (XAS) and resonance photoemission spectroscopy (RPES). Mn L$_2$-edge XAS indicates that the doped Mn atoms have a valence 2+ and strongly hybridize with the 4p orbitals of the tetrahedrally coordinating As ligands. The Mn 3d partial density of states obtained by RPES shows a peak around 4 eV and is relatively high between 0 and 2 eV below the Fermi level ($E_F$) with little contribution at $E_F$, similar to that of the archetypal DMS Ga$_{1-x}$Mn$_x$As. This energy level creates a $d^5$ electron configuration with $S = 5/2$ local magnetic moments at the Mn atoms. Hole carriers induced by K substitution for Ba atoms go into the top of the As 4p valence band and are weakly bound to the Mn local spins. The ferromagnetic correlation between the local spins mediated by the hole carriers induces ferromagnetism in Ba$_{1-x}$K$_x$(Zn$_{1-y}$Mn$_y$)$_2$As$_2$.

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Diluted magnetic semiconductors (DMSs) have received much attention due to the possibility of utilizing both charge and spin degrees of freedom in electronic devices [1–5]. In order to realize functional spintronics devices, it is important to have full control of the carrier density and ferromagnetic Curie temperature ($T_C$). Prototypical DMS systems such as Ga$_{1-x}$Mn$_x$As, In$_{1-x}$Mn$_x$As, and Ga$_{1-x}$Mn$_x$N, however, show severely limited chemical solubility due to the substitution of divalent Mn atoms for the trivalent Ga or In sites. Besides, the simultaneous doping of charge and spin induced by Mn substitution prevents us from optimizing the charge and spin densities independently, although the tuning of the charge density by applying a gate voltage is possible and can be used to control $T_C$ [6].

A newly found DMS, Ba$_{1-x}$K$_x$(Zn$_{1-y}$Mn$_y$)$_2$As$_2$ [7] (Mn-BaZn$_2$As$_2$), is isostructural to "122"-type iron-based high-temperature superconductors [8] and has a $T_C$ as high as 230 K [9]. This material has an advantage that the charge reservoir Ba layer and the ferromagnetic ZnAs layer are spatially separated, which allows us to control the amount of hole carriers by K substitution to the Ba layer and that of magnetic elements by substituting Mn to the ZnAs layer rather independently. In addition, the substitution of Mn atoms for isovalent Zn atoms enables us to circumvent the difficulty of limited chemical solubility in Ga$_{1-x}$Mn$_x$As and related DMSs, which makes it possible to obtain bulk specimens. An anomalous Hall effect observed in Mn-BaZn$_2$As$_2$ [7] provides evidence that the ferromagnetism here is intrinsic as in Ga$_{1-x}$Mn$_x$As [10,11]. This series of DMSs, together with the “111”-type materials Li(Zn,Mn)As [12] and Li(Zn,Mn)P [13], opens up possibilities for next generation spintronics devices. To achieve this goal, it is important to investigate the electronic and magnetic structure of Mn-BaZn$_2$As$_2$ and clarify the advantages of this material as compared with archetypal Mn-doped-based DMS materials such as Ga$_{1-x}$Mn$_x$As and In$_{1-x}$Mn$_x$As.

In the present Rapid Communication, we have performed x-ray absorption spectroscopy (XAS) and resonance photoemission spectroscopy (RPES) measurements on Mn-BaZn$_2$As$_2$ ($x = 0.3$, $y = 0.15$, $T_C = 180$ and 230 K). Polycrystalline samples were synthesized under high pressure by the method described in Ref. [7]. XAS measurements for samples with $T_C = 230$ K were performed at the Dragon Beamline BL-11A of National Synchrotron Radiation Research Center (NSRRC), Taiwan. The spectra were taken in the total-electron yield (TEY: probing depth∼5 nm) mode. The monochromator resolution was $E/\Delta E > 10000$ and the x rays were circularly polarized. The samples were filed in situ before the measurements to obtain fresh surfaces. RPES experiments for samples with $T_C = 180$ K were performed at Beamline 2C of Photon Factory, High-Energy Accelerator Research Organization. RPES experiments were done before the synthesis of the Tc = 230 K samples [9]. Calibration of the Fermi level ($E_F$) was achieved using the $E_F$ of gold, which was in electrical contact with the samples. Incident photon energies from 635 to 643 eV were linearly polarized. In order to gain further insight into the electronic structure of the host semiconductor BaZn$_2$As$_2$, we have performed density-functional theory (DFT) calculations.

To understand the electronic structure of the host semiconductor, we performed band-structure calculations on BaZn$_2$As$_2$ using the WIEN2k package [14]. Figure 1(a) shows the calculated band structure and the density of states (DOS). BaZn$_2$As$_2$ has space group I4/mmm and the first Brillouin zone is shown in the inset of the right panel. The calculations were done using the experimentally determined tetragonal
lattice constants $a = 4.12 \, \text{Å}$, $c = 13.58 \, \text{Å}$ [7], and the arsenic height $h_{\text{As}} = 1.541 \, \text{Å}$ [15]. First we tried the local density approximation (LDA) and generalized gradient approximation (GGA) exchange functionals [16, 17], but they gave overlapping conduction and valence bands, inconsistent with the semiconducting electrical conductivity with a band gap of 0.23 eV [18]. This is the well-known underestimation of the band gap in LDA and GGA, and therefore we next employed the so-called modified Becke-Johnson exchange potential (mBJ) implemented in the WIEN2K program [19] with a standard mixing factor for the exact-exchange term of 0.25 [20]. We thus approximated the exact-exchange term of 0.25 [20].

We thus employed the mBJ potential. The lattice parameters for BaZn$_2$As$_2$ calculated using the modified Becke-Johnson exchange potential. The line shapes of BaZn$_2$As$_2$ compared with those of some reference systems. The line shapes of BaZn$_2$As$_2$ are intermediate between two DMS systems, Ga$_{0.922}$Mn$_{0.078}$As [22] (GaMnAs) and Ga$_{0.958}$Mn$_{0.042}$N [23] (GaMnN), indicating that the Mn atoms take a valence of 2+ and that Mn 3d orbitals strongly hybridize with the surrounding As 4p orbitals as in GaMnAs and GaMnN. From the shoulder structures around $h = 640$ and 643 eV, which are more pronounced than in GaMnAs and weaker than in GaMnN, we see that the strength of hybridization is weaker than in GaMnAs but stronger than in GaMnN. The line shape has a more localized nature than the metallic compounds Mn metal [24] and Mn doped into BaFe$_2$As$_2$ [25]. However, it does not have the clear multiplet structures seen in the spectra of LaMnO$_3$ and MnO [26], consistent with the semimetallic conductivity in Mn-BaZn$_2$As$_2$.

In order to extract the local electronic structure of the doped Mn, we performed RPES experiments using photon energies around the Mn $L_3$ edge. In RPES, one makes use of the property that the cross section of photoemission from an atomic orbital is enhanced by quantum-mechanical interference between the direct photoemission of a $dn$ electron, $3d^n + h\nu \rightarrow 3d^{n-1} + e^-$, and absorption followed by a Coster-Krönig transition $2p^63d^n + h\nu \rightarrow 2p^73d^{n+1} \rightarrow 2p^53d^{n-1} + e^-$ [27, 28]. This effect is useful in extracting the 3d partial density of states (PDOS) of a transition element in solids. Following the observed x-ray absorption spectra, we measured the valence-band photoemission spectra with photon energies from the off-resonance to on-resonance regions. A series of photoemission spectra taken with a small photon energy interval enables us to clearly identify the resonance enhancement of Mn 3d-related photoemission features.

Figure 3(a) shows the valence-band spectra taken with photon energies in the Mn $L_3$ absorption region. The photon energies used are shown by the arrows on the XAS spectrum in Fig. 3(b). The high DOS of the Zn 3d states is clearly observed $\sim 10$ eV below $E_F$. Note that, regardless of hole doping in Mn-BaZn$_2$As$_2$, the Zn 3d peak is located at $\sim 10$ eV. (In DFT calculations, it is calculated to be $\sim 7.5$ eV; see Fig. 1. A similar discrepancy of the Zn 3d energy level between DFT and photoemission is also found.
FIG. 3. (Color online) (a) Evolution of the valence-band photoemission spectrum of Mn-BaZn$_2$As$_2$ with photon energies $h\nu = 635$–$643$ eV. Excitation photon energies are shown by the arrows on the XAS spectrum in (b).

In Zn-doped BaFe$_2$As$_2$ [29,30], photon-energy-independent peaks observed at $-15$ and $-18$ eV originate from the Ba 5$p$ and K 3$p$ orbitals, respectively. Most importantly, one can see the enhancement of spectral features in $-8$ to $0$ eV as the photon energy approaches the on-resonance energy at 638.5 eV and the subsequent reduction of the spectral weight at higher photon energies.

In order to highlight the resonance enhancement of the Mn 3$d$-derived spectral weight, we show the on-off the difference spectra in Fig. 4. The off-resonance spectrum ($h\nu = 635$ eV) at the bottom of Fig. 4(a) has been subtracted from each spectrum. The strongest enhancement around the Mn $L_3$ edge ($h\nu = 638.5$ eV) is seen around $-4$ eV. Vertical bars indicate a constant kinetic energy characteristic of the Auger emission.

By subtracting the off-resonance spectra from the on-resonance spectra, we have deduced the PDOS of Mn 3$d$ orbitals as shown in Fig. 4(b). The DOS is low at $E_F$, finite between $-2$ eV and $E_F$, and takes a maximum at $-4$ eV. The Mn 3$d$ spectral weight is widely distributed from $\sim -10$ to $-2$ eV. The deduced PDOS is compared with that of Ga$_{0.957}$Mn$_{0.043}$As [31] in Fig. 4(c). Except that the peak in Ga$_{0.957}$Mn$_{0.043}$As is about 0.4 eV deeper than that of Mn-BaZn$_2$As$_2$, the overall spectral features are quite similar, indicating that the electronic states of doped Mn are alike in these two DMS systems. This similarity originates from the same chemical valence 2+ of the Mn atoms and the tetrahedral coordination by the As 4$p$ orbitals.

From the obtained energy levels, we gain insight into the localization of hole carriers doped by K substitution in Mn-BaZn$_2$As$_2$. The Zn 3$d$ orbital is located as deep as 10 eV below $E_F$ and thus cannot accommodate holes. Also, since the Mn 3$d$ PDOS has a maximum at $-4$ eV and very little contribution at $E_F$, they cannot accept holes either. Therefore, holes are predominantly introduced into the valence band composed mainly of the As 4$p$ states. Thus Mn atoms have a valence of 2+ as observed in the XAS spectrum in Fig. 2, and the local magnetic moments with $S = 5/2$ are formed in the presence of Hund’s coupling between electrons of $d^5$ configuration [33].

The formation of the local magnetic moments affects the hole mobility. Upon K doping into the parent compound ($x = y = 0$), the resistivity at $T = 0$ significantly decreases from $1 \times 10^4$ $\Omega$ cm ($x = 0$) to $5 \times 10^{-1}$ $\Omega$ cm ($x = 0.1$) [7]. On the other hand, it does not radically decrease in samples with $y = 0.1$, from 4 $\Omega$ cm ($x = 0$) to 2 $\Omega$ cm ($x = 0.3$). This behavior indicates that, while hole carriers introduced into the As 4$p$-derived valence band are originally itinerant, they are weakly bound to the local magnetic moments and lose mobility in the Mn-doped samples.

The ferromagnetic correlation between the local $S = 5/2$ spins of Mn$^{2+}$ ions is considered to be mediated by the holes weakly bound to them. In generating ferromagnetism, the positions of the impurity level and $E_F$ are key parameters. A combined approach of density-functional theory and quantum Monte Carlo method [34] on the Haldane-Anderson model [35,36] showed that, when $E_F$ is located between the bound impurity state and the valence-band maximum of GaMnAs, a long-range ferromagnetic correlation between
the impurities develops as a result of the antiferromagnetic impurity-host coupling and that it is enhanced with decreasing temperature. Indeed, a recent resonance angle-resolved photoemission study on GaMnAs [37] reveals the presence of a nondispersive impurity band in the vicinity of the valence-band maximum as a split-off Mn-impurity state. Given that the valence-band top of BaZn2As2 is higher than that of GaAs, Mn-BaZn2As2 seems to satisfy the above condition. However, in order to precisely determine the mechanism of ferromagnetism in Mn-BaZn2As2, it is essential to experimentally investigate the properties of the impurity state. Optical and angle-resolved photoemission spectroscopy studies on the new series of DMSs are desired in future studies.

In conclusion, by using XAS and RPES techniques, we have studied the electronic structure of Ba1−xKx(Zn1−yMny)2As2, in particular, that related to the Mn 3d states. The Mn L2,3-edge XAS spectrum indicates that the doped Mn atoms have a valence 2+ and are strongly hybridized with the As 4p orbitals as in archetypal DMSs GaMnAs. The Mn 3d PDOS obtained by RPES shows a peak around $E_F = 4$ eV and is relatively high between $E_F = 0$ and 2 eV, with little contribution at $E_F$. These electronic states below $E_F$ lead to the $d^5$ electron configuration of Mn atoms with the local magnetic moment of $S = 5/2$. From a comparison between DFT band dispersions of the host semiconductor BaZn2As2 and the experimental Mn 3d PDOS of Mn-BaZn2As2, we conclude that doped holes go into the top of the As 4p-derived valence band and are weakly bound to the Mn local spins. The ferromagnetic correlation between the local spins mediated by the hole carriers induces ferromagnetism in $K_x(\text{Zn}_{1-y}\text{Mn}_y)_2\text{As}_2$.

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[33] The saturated magnetic moment of 1–2μB per Mn in Mn-BaZn2As2 reported in Ref. [7] may be caused by partial antiferromagnetic coupling between the S = 5/2 local spins.