Pressure effect on the magnetism of the diluted magnetic semiconductor (Ba$_{1-x}$K$_x$)(Zn$_{1-y}$Mn$_y$)$_2$As$_2$ with independent spin and charge doping


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We used x-ray magnetic circular dichroism (XMCD) to probe the ferromagnetic properties of As $p$-symmetric (4$p$) states in the recently synthesized diluted magnetic semiconductor (Ba$_{1-x}$K$_x$)(Zn$_{1-y}$Mn$_y$)$_2$As$_2$ system under ambient- and high-pressure conditions. The As $K$-edge XMCD signal scales with the sample magnetization (dominated by Mn) and scales with the ferromagnetic ordering temperature $T_c$, and hence it is representative of the bulk magnetization. The XMCD intensity gradually decreases upon compression and vanishes at around 25 GPa, indicating quenching of ferromagnetism at this pressure. Transport measurements show a concomitant increase in conductivity with pressure, leading to a nearly metallic state at about the same pressure where magnetic order collapses. High-pressure x-ray diffraction shows an absence of structural transitions to 40 GPa. The results indicate that the mobility of doped holes, probed by both transport and x-ray absorption spectroscopy (4$p$ band broadening), is intimately connected with the mechanism of magnetic ordering in this class of compounds and that its control using external pressure provides an alternative route for tuning the magnetic properties in diluted magnetic semiconductor materials.

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I. INTRODUCTION

Diluted magnetic semiconductor (DMS) materials, combining the tunability of charge and spin degrees of freedom, offer a rich variety of remarkable properties that attract extensive interest in materials science as well as opening prospects for the design of new functional spintronic devices [1–5]. Rapid progress on DMS research started in the 1990s, to a large extent, owing to the development of crystal growth methods far from thermal equilibrium, especially by molecular beam epitaxy (MBE) techniques. In the Mn-doped III–V DMS systems, Mn substituting for the trivalent cation (Ga) is simultaneously an acceptor and a source of magnetic moments. This dual role of Mn presents an obstacle to both material synthesis and theoretical understanding. The recently discovered Mn-doped I–II-V semiconductor Li$_{1+x}$Zn$_{1-y}$Mn$_y$As [6] and Mn-doped II–II-V semiconductor (Ba$_{1-x}$K$_x$)(Zn$_{1-y}$Mn$_y$)$_2$As$_2$ [7], belonging to a new generation of bulk ferromagnets, exhibit certain advantages over the (III, Mn)V–based materials. Key differences exist between these new types of DMS and (III, Mn)V materials like (Ga, Mn)As in both the mechanism of spin and charge injection and the intricacies of material synthesis. In semiconductor (Ba$_{1-x}$K$_x$)(Zn$_{1-y}$Mn$_y$)$_2$As$_2$, holes are induced by (Ba$^{2+}$,K$^{1+}$) replacement independent of spin doping, which is induced via (Zn$^{2+}$,Mn$^{2+}$) replacement. Bulk samples display ferromagnetic ordering with Curie temperature, $T_c$, up to 230 K [8], which has been significantly enhanced from $T_c \sim 50$ K of Li$_{1+x}$Zn$_{1-y}$Mn$_y$As and is higher than the highest $T_c \sim 200$ K for (Ga, Mn)As [9].

The physical properties of DMS materials are strongly sensitive to external factors such as magnetic field, temperature, and pressure. In addition to the crystal structure, the magnetism plays a key role in determining the physical properties. Therefore, a key route to obtaining further insight on the underlying mechanism leading to magnetic order in DMS materials is via control of the ferromagnetic response with tunable thermodynamic conditions. In this context, external pressure offers interesting opportunities [10], because it can modify both electronic bandwidths and band gaps in DMSs without introducing chemical disorder inherent to doping, and therefore it is an effective method to draw out the complicated interplay among structural, magnetic, and electronic degrees of freedom in these novel ferromagnets.

Recent theory [11] of Mn-doped II–II-V semiconductors, e.g., (Ba$_{1-x}$K$_x$)(Zn$_{1-y}$Mn$_y$)$_2$As$_2$, predicts that the magnetic ordering emerges from the competition between the short-range antiferromagnetic (superexchange) interaction and a longer-range ferromagnetic interaction mediated by the itinerant As holes. This model also predicts an induced magnetic moment on As atoms that couples antiparallel to the Mn 3$d$ moments. The general understanding for most common (III, Mn)V–based DMSs invokes As-derived valence-band states [12,13] as mediators of ferromagnetic interactions. However, for the new-generation Mn-doped II–II-V semiconductors, the details of the electronic band structure and the role of As mediating (hole) states remain unresolved both in...
experiment and theory. Thus, it is necessary to get in-depth insight into the role of As valence-band states to verify the theory of carrier-mediated long-range ferromagnetic order and to identify the nature of the mediating states.

The combination of hard x-ray magnetic circular dichroism (XMCD) and diamond anvil cell techniques has proven to be a valuable way to study stability of ferromagnetism to applied pressure [14–18]. In this paper, we report the pressure effect on the electronic properties of (Ba1−xKx)(Zn1−yMny)2As2 using XMCD at the As K-edge. XMCD is the difference in x-ray absorption (XAS) measured with right (μ+) and left (μ−) circularly polarized photons. The transfer of photon angular momentum to the excited photoelectron allows the orbital magnetization of the p-symmetric (4p) states to be probed. The K-edge XMCD signal of first-row transition metal atoms Fe, Co, and Ni [19–21], as well as Mn in (Ga, Mn)As and (In, Mn)As [22,23], arises from polarization of 4 magnetic sites. This hybridization is also the source of As 4 states produced by 4 by XMCD at the As K-edge. XMCD signals indicate that the induced As orbital moment is antiparallel to the total moment [24], which is dominated by the Mn 3d spin moment. Due to the electric dipole selection rules and the Pauli exclusion principle, an absorption spectrum from any state of the ground configuration \( n \) of the ion to any state of the final configuration \( c^{n+1} \) (c denotes a core hole) is determined by the partial densities of unoccupied states with l character and their corresponding transition probabilities. The occurrence of an XMCD signal at the lower-energy side of the absorption edge indicates that the hole carriers introduced by K doping at Ba sites required for ferromagnetism reside on As 4p states near the valence-band edge. The doped charge (hole) carriers lead to a downward shift of the Fermi-level, \( E_f \), which results in unoccupied states near \( E_f \) with As 4p character. To study the relationship between the As XMCD and the ferromagnetic ordering temperature \( T_c \), we measured XMCD spectra of (Ba1−xKx)(Zn1−yMny)2As2 with different doping levels under the same conditions (\( H = 4 T, T = 2 K \)), as shown in Fig. 1(b). It is clear that the As XMCD intensity correlates strongly with \( T_c \).

By applying the s (l = 0) core level orbital magnetization sum rule [25–27], the integrated XAS and XMCD intensities can be related to the element- and shell-selective orbital magnetic moment. For the K edge, the 4p orbital moment per hole is given by

\[
\frac{\int_{E_f}^{E_i} dE [\mu^+(E) - \mu^-(E)]}{\int_{E_f}^{E_i} dE [\mu^+(E) + \mu^0(E) + \mu^-(E)]} = - \frac{\langle L_z \rangle_p}{n_p^0},
\]

where \( n_p^0 \) is the number of holes in the p valence shell, and \( \langle L_z \rangle_p \) is the p-projected ground state orbital magnetic moment. The transition from a 1s core to the continuum states of an isolated As ion was modeled by an arctan function and subtracted from the normalized isotropic, \( \mu^0 \),

II. RESULTS AND DISCUSSION

Polycrystalline (Ba1−xKx)(Zn1−yMny)2As2 samples were synthesized using the arc-melting solid state reaction method [7] and ground into fine powder before experiment. The samples were mounted on tapes for low-temperature experiments under ambient-pressure condition. For the high-pressure measurements, the sample was mixed with silicon oil and loaded into the diamond anvil cell together with Ruby markers for online pressure calibration at low temperature. A cryogenic superconducting magnet with a bore large enough to accommodate a membrane-driven CuBe diamond anvil cell (DAC) was used, allowing application of high fields (up to 6.5 T) and in situ control of pressure. For the XMCD signal, x-ray helicity was modulated at 13.1 Hz, the x-ray beamline uses a diamond phase retarder to convert the source (APS) at Argonne National Laboratory. This hard x-ray magnetic circular dichroism (XAS) measured with right (μ+) and left (μ−) circularly polarized photons. The transfer of photon angular momentum to the excited photoelectron allows the orbital magnetization of the p-symmetric (4p) states to be probed by XMCD at the As K-edge.
and to the XMCD peak position. The agreement in coercivity measured at a fixed energy from SQUID are shown in Fig. 2. The XMCD signal was along with the temperature-dependent XMCD data taken at the As magnetic ordering of the bulk sample. The hysteresis and magnetometry and hence is strongly connected with the by superconducting quantum interference device (SQUID) XMCD closely follows the total magnetization measured on the external magnetic field- and temperature-dependent XMCD sample magnetization (dominated by Mn), we measured the hysteresis loops at ambient pressure, taking zero field cooling, in $H = 500$ Oe. All data are normalized to unity at the highest magnetic field or lowest temperature. The SQUID data were collected on the same sample used in the XMCD measurements.

XAS data before the integration. For the $x = 0.25$, $y = 0.05$ sample at ambient pressure, taking $n_{h}^{s} = 0.125$ hole/As, we determined the value of the orbital moment in the As 4$p$ band to be $\langle L_z \rangle_p = -0.000106(8)$. The As 4$p$ spin polarization (due to $p - d$ hybridization) together with the spin-orbit interaction give rise to the orbital polarization in the 4$p$ band, which is antiparallel to the net magnetization (dominated by Mn). Theoretical calculations [11] show that As atoms acquire spin polarization that is opposite to Mn polarization. We conclude that spin and orbital moments are parallel and opposite to the Mn magnetic moments. The orbital magnetic moment per As ion obtained from sum-rule analysis shows an approximately linear relationship with increasing $T_c$ [Fig. 1(c)]. The doping-dependent measurements indicate that the As orbital moment (polarization of charge carriers) is involved in mediating magnetic ordering.

To confirm that the As K-edge XMCD signal scales with the sample magnetization (dominated by Mn), we measured the external magnetic field- and temperature-dependent XMCD on the $x = 0.25$, $y = 0.05$ sample at ambient pressure. The XMCD closely follows the total magnetization measured by superconducting quantum interference device (SQUID) magnetometry and hence is strongly connected with the magnetic ordering of the bulk sample. The hysteresis and temperature-dependent XMCD data taken at the As K-edge, along with the $M$-$H$ plot and zero-field-cooled $M$-$T$ plot from SQUID are shown in Fig. 2. The XMCD signal was measured at a fixed energy $E = 11,870.5$ eV corresponding to the XMCD peak position. The agreement in coercivity and $T_c$ is robust, indicating that the As K-edge XMCD is representative of the bulk magnetization. These results further prove that the polarized As moments are induced by proximity to the magnetically ordered Mn ions in the $(\text{Ba}_{1-x} \text{K}_x)(\text{Zn}_{1-y} \text{Mn}_y)_2\text{As}_2$ system. This validates the conclusions in Ref. [11] and Ref. [28] and supports the model of carrier-mediated ferromagnetic ordering involving As-derived valence-band states.

Figure 3(a) shows the high-pressure As XMCD spectra taken at $T = 2$ K and magnetic field of 2 T for the $x = 0.25$, $y = 0.05$ sample. The overall intensity of the spectra diminishes as the pressure increases, and only a remnant feature remains at 25 GPa. The relative XMCD peak intensities ($E = 11,870.5$ eV) measured on compression and decompression are plotted in Fig. 3(b). The pressure-induced quenching of the As XMCD signal is reversible. When decompressed to $\sim 11$ GPa, the signal returns to a value close to that observed on compression. As discussed above, the polarization of the As $p$ band is strongly correlated with $T_c$, namely, the strength of ferromagnetic coupling between Mn atoms. Generally, the source of this indirect exchange interaction can be described as [29,30]: (i) a charge carrier is polarized by the $p-d$ exchange interaction with a Mn$^{2+}$ ion at a given site, and (ii) propagation of the polarized charge carrier mediates the interaction with a Mn$^{2+}$ ion at another site. Therefore, the decrease of As XMCD intensity under pressure indicates the weakening of the ferromagnetic exchange between Mn ions. To directly verify this conclusion, we measured the temperature dependence of As XMCD at the decompressed pressure of 11 GPa [Fig. 3(c)], where the XMCD intensity is reduced by about a factor of 2 from its ambient-pressure value [Fig. 3(b)]. As expected, the ordering temperature decreases significantly. The onset
temperature of magnetic order takes place at about 100 K, compared to 150 K at ambient pressure [Fig. 2(b)].

We also studied the pressure effect on the electrical transport properties of the $x = 0.25$, $y = 0.05$ sample. Technical details for these measurements can be found in Ref. [31]. The sample undergoes a semiconductor to metal-like transition upon compression, as shown in Fig. 4(a). The zero-field resistance measured at $T = 2$ K as a function of pressure is plotted in Fig. 4(b). The resistivity rapidly decreases with pressure, and an increase of more than one order of magnitude in conductivity is observed at 24 GPa. Since changes in crystal symmetry with pressure could dramatically influence the electronic degrees of freedom, we conducted in-situ high-pressure x-ray diffraction (XRD) experiments at the 16 BM-D beamline of the Advanced Photon Source at Argonne National Laboratory ($T = 300$ K). Rietveld refinements of the high-pressure data were performed with the GSAS package [32,33]. The $(Ba_{1-x}K_x)(Zn_{1-y}Mn_y)_2As_2$ DMS materials crystallize into a tetragonal ThCr$_2$Si$_2$-type structure (space group $I4/mmm$) at ambient pressure [7]. We found no structural phase transitions to 40 GPa, indicating that the suppression of magnetic order and concomitant emergence of a metal-like state under pressure are not a result of change in lattice symmetry (see Fig. S1 in the Supplemental Material [34]). Figure 4(c) shows that the unit cell volume is reduced by 23% at 24 GPa (bulk modulus $B = 45$ GPa). The compression of the lattice increases electronic bandwidth and enhances carrier mobility, as clearly seen in the transport measurements. The pressure experiments show that ferromagnetism and carrier mobility are strongly correlated. The spin polarization of hole carriers decreases as they become more itinerant, indicating that carrier mobility is intimately connected to the mechanism behind ferromagnetic ordering. Similar behavior was also observed in some high-temperature, weakly ferromagnetic iridate systems (see Ref. [35]). The electronic structure and magnetism are closely coupled to the lattice volume, which affects electronic bandwidth, hole mobility, and the strength of magnetic (exchange) interactions.

We now examine the XAS data in order to characterize the evolution of the As $4\rho$ band under pressure. Figure 5(a) displays the pressure-dependent “white lines” [shadowed area in Fig. 1(a)] obtained after subtracting the continuum (edge-step) contributions to the isotropic XAS ($T = 2$ K) spectra. Under compression, a gradual broadening of the $4\rho$ band is observed. The bandwidth is 33% larger at 25 GPa relative to ambient pressure, while the change of integrated area is only a few percent [Fig. 5(b)]. This indicates that the number of holes does not change significantly with pressure while hole mobility (bandwidth) does. These results show that bands derived from outer-shell $4\rho$ orbitals are quite compressible and that lattice compression alone can precipitate drastic changes in the ground state, namely, a semiconductor to metal-like transition accompanied by loss of ferromagnetic order. We conclude that the magnetic ordering of these materials is critically linked to the mobility of doped carriers. The pressure experiments are unique in that they allow isolation of the effect of hole mobility (bandwidth) on the exchange mechanism at fixed doping. This is of course impossible to achieve in doping experiments, where dopants add holes but also disorder, in addition to changes in bandwidth. It is worth noticing that even the highest achievable doping levels ($x = 0.3$) result in a semiconducting state at ambient pressure [7].

**FIG. 5.** (a) Background-subtracted “white line” peaks in As $K$-edge data at $T = 2$ K under different pressures for $(Ba_{0.75}K_{0.25})(Zn_{0.95}Mn_{0.05})_2As_2$. (b) Black solid points indicate white line peak width (bandwidth) under pressure, and blue solid points are the integrated area (number of holes) with pressure; all data are normalized to their $P = 1$ bar values. Dashed lines are guides to the eye.
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