

Ferromagnetism at 230 K in $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ diluted magnetic semiconductor

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Abstract We report the ferromagnetism with Curie temperature T_c at 230 K in a new diluted magnetic semiconductor (DMS) $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ isostructural to ferropnictide 122 superconductors synthesized via low temperature sintering. Spin is doped by isovalence substitution of Mn^{2+} for Zn^{2+} , while charge is introduced by heterovalence substitution of K^{1+} for Ba^{2+} in $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ DMS, being different from $(\text{Ga},\text{Mn})\text{As}$ where both spin & charge are induced simultaneously by heterovalence substitution of Mn^{2+} for Ga^{3+} . The $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ DMS shows spontaneous magnetization following $T^{3/2}$ dependence expected for a homogeneous ferromagnet with saturation moment $1.0\mu_B$ for each Mn atom.

Keywords Diluted magnetic semiconductors · Decoupled spin charge doping · High Curie temperature

Diluted magnetic semiconductors (DMS) have received much attention due to their potential application in spintronics [1–5]. In typical systems based on III-V semiconductors, such as $(\text{Ga},\text{Mn})\text{As}$, $(\text{In},\text{Mn})\text{As}$ or $(\text{Ga},\text{Mn})\text{N}$, substitution of divalent Mn atoms into trivalent Ga (or In) sites leads to severely limited chemical solubility, resulting in metastable specimens only available as epitaxial thin films. The hetero-valence substitution, which simultaneously

dopes both charges and spin, makes it difficult to individually control each quantum freedom.

Recently, a new type DMS $\text{Li}(\text{Zn},\text{Mn})\text{As}$ (termed “111” following the chemical compositions ration) with decoupled charge & spin doping was discovered [6], with charges injected via off-stoichiometry of Li and spins by the isovalent $(\text{Zn}^{2+},\text{Mn}^{2+})$ substitutions, showing a Curie temperature up to $T_c = 50$ K. Comparing with classical DMS such as $(\text{Ga},\text{Mn})\text{As}$, the lower T_c of the new “111” system is an obstacle for possible application. More recently, a new ferromagnetic DMS $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$ (named “122” type following the chemical ration) system sharing the same structure with “122” type iron pnictide superconductors [7] was reported [8]. Via (Ba,K) substitution to dope hole carriers and (Zn,Mn) substitution to supply magnetic moments, the systems with 5 %–15 % Mn doping exhibit ferromagnetic order with T_c up to 180 K [8]. The μSR experiments indicates that the magnetism is homogenous intrinsic property [9].

One of challenges to possible application for DMS is approaching T_c near room temperature. Given the fact that the Curie temperature of $(\text{Ga},\text{Mn})\text{As}$ could be highly enhanced through increasing carrier density by low temperature annealing [10, 11], optimizing synthesis condition may also pave the way to further improve T_c in $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$ system as well. Here, we report ferromagnetism at 230 K in new diluted magnetic semiconductor $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$, with the Curie temperature higher than the record T_c for $(\text{Ga},\text{Mn})\text{As}$ [11].

Previous study shows that $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ demonstrates the highest T_c for the $(\text{Ba}_{1-x}\text{K}_x)(\text{Zn}_{1-y}\text{Mn}_y)_2\text{As}_2$ system [8]. We hence choose $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ as the target composition in this study. Polycrystals of $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ were synthesized using the arc melting solid-state reaction method.

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The starting materials, namely, BaAs, K, ZnAs, and high-purity Mn powders, were mixed according to the nominal composition of $(\text{Ba,K})(\text{Zn,Mn})_2\text{As}_2$. The mixture was sealed inside an evacuated tantalum tube that is, in turn, sealed inside an evacuated quartz tube. To avoid the volatile of K at high temperature hence to increase K contents in the sample & consequently increase carrier density, the mixture was heated under $650\text{ }^\circ\text{C}$ for 60 h, a hundred degree lower than the boiling temperature of Potassium element. Samples were characterized by X-ray powder diffraction with a Philips X'pert diffractometer using Cu K-edge radiation. The DC magnetic susceptibility was characterized using a superconducting quantum interference device magnetometer (Quantum Design, Inc.), whereas the electronic-transport were measured using a physical property measuring system.

As shown in Fig. 1, the sample crystallizes in the tetragonal ThCr_2Si_2 structure, isostructural to “122” type iron pnictide superconductors. Based on X-ray diffraction patterns collected within a 2θ range from 10° to 80° , the least-squares method was used to determine the lattice parameters with $a = 4.130\text{ \AA}$ and $c = 13.509\text{ \AA}$, respectively.

Figure 2(a) shows temperature-dependent magnetization in zero-field-cooling (ZFC) and field cooling (FC) modes under 500 Oe for $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ polycrystal, respectively. There are clear signatures of ferromagnetic order in the curves at the critical temperature (T_c) 230 K. The hysteresis curves $M(H)$ are shown in the inset of Fig. 2(a) for $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ at $T = 2\text{ K}$.

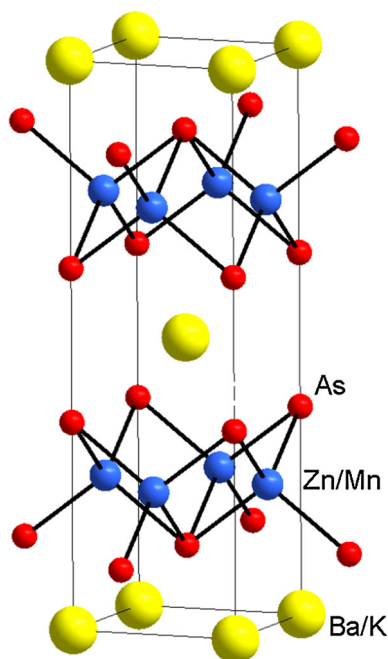


Fig. 1 Crystal structure of $(\text{Ba,K})(\text{Zn,Mn})_2\text{As}_2$ identical to tetragonal ThCr_2Si_2 , isostructural to “122” type iron pnictide superconductors

The saturation moment is $1\mu_B$ per Mn atom, comparable with that of $(\text{Ga,Mn})\text{As}$ [1], $\text{Li}(\text{Zn,Mn})\text{As}$ [6], and $(\text{Ba,K})(\text{Zn,Mn})_2\text{As}_2$ [8]. In Fig. 2(b) the spontaneous magnetization of $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ under 5 Oe in low temperature shows $T^{3/2}$ dependence expected for a homogeneous ferromagnet, as observed in $(\text{Ga,Mn})\text{As}$ [12].

As depicted in Fig. 3, the resistivity curve of $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$, similar to that of $(\text{Ga,Mn})\text{N}$ [13], exhibits a small increase at low temperatures due presumably to spin scattering of carriers caused by Mn dopants. As indicated, the carrier-mediated and RKKY-like interaction induced ferromagnetism could also be observed in insulating samples close to the metal-insulator transition [1]. Different from the case of metallic $(\text{Ga,Mn})\text{As}$ [14, 15] that shows negative magnetoresistance at $T > T_c$ which achieves its maximum near T_c probably owing to the rapid polarization of the Mn spins, clear signature of the ferromagnetic order of $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ is evidenced by the obvious negative magnetoresistance below T_c . With decreasing temperature, the negative magnetoresistance is greatly enhanced, showing different magnetic field dependence relationship. At $T = 10\text{ K}$, an obvious hysteresis is observed in magnetoresistance curve, showing a consistent coercive force in $M(H)$ curve. The small positive magnetoresistance observed in low magnetic field is most probably caused by the rotation of spins from its original direction to the magnetic field direction [15].

In this $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ sample sintered at $650\text{ }^\circ\text{C}$, the carrier concentration is about $8 \times 10^{20}\text{ cm}^{-3}$ as estimated from Hall measurement at 250 K that is enhanced a quarter than that of the sample sintered at $750\text{ }^\circ\text{C}$ with T_c 180 K [8] as shown in Fig. 4. It is argued that in low temperature annealed $(\text{Ga,Mn})\text{As}$, the increase of carrier density probably accounts for the enhancement of Curie temperature [10–12]. Since potassium becomes melting at very low temperature ($\sim 63\text{ }^\circ\text{C}$) & boiling at $750\text{ }^\circ\text{C}$ there will be a certain amount of potassium becomes evaporation during sintering at high temperature. As we addressed that the hetero valence substitution of K for Ba provides carriers to mediate spin orientation in $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$, the higher potassium concentration in the lattice & hence higher carrier concentration would be favorable to enhance ferromagnetism. The low temperature sintering well below the boiling temperature of Potassium element would certainly suppress its volatility, hence leading to increase of carrier density. The enhanced carrier density thus account for high Curie temperature in the $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ synthesized at low temperature. We found that the sintering temperature at $650\text{ }^\circ\text{C}$ is the threshold in our experiments in order to form the $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ structure.

In the present “122” DMS ferromagnet $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$, semiconducting BaZn_2As_2 [8],

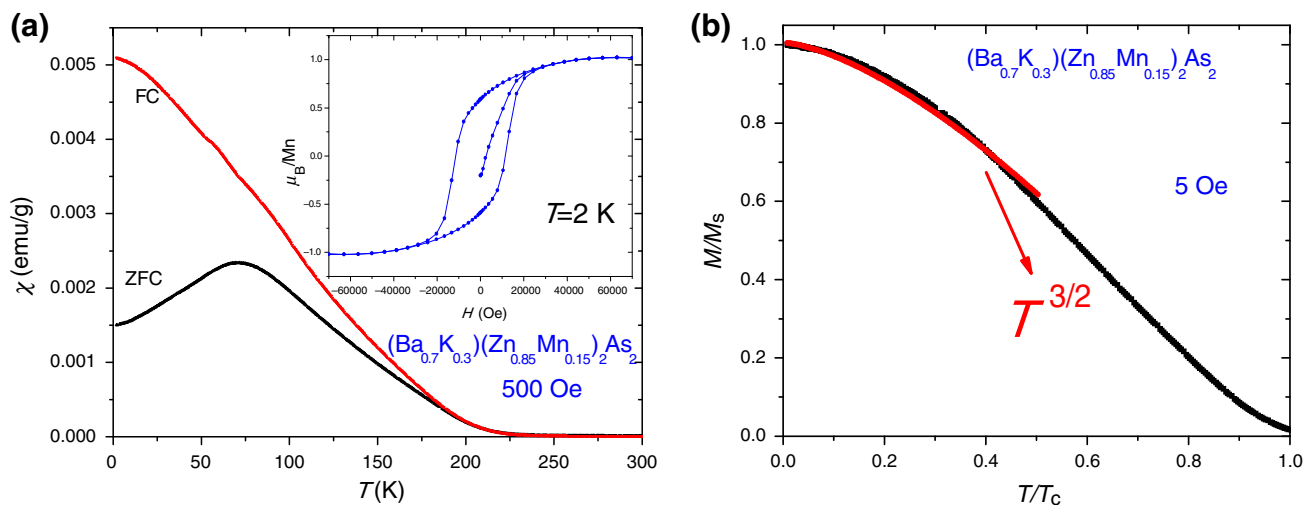


Fig. 2 **a** magnetization measured in $H = 500$ G in $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ at both zero field cooling (ZFC) and field cooling (FC) modes, with Curie temperature (T_c) 230 K. Inset: The isothermal magnetic hysteresis curve $M(H)$, measured in the external field H up to $7T$; **b** the spontaneous magnetization curve under 5 Oe of $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$, showing $T^{3/2}$ dependence in low temperature expected for a homogeneous ferromagnet

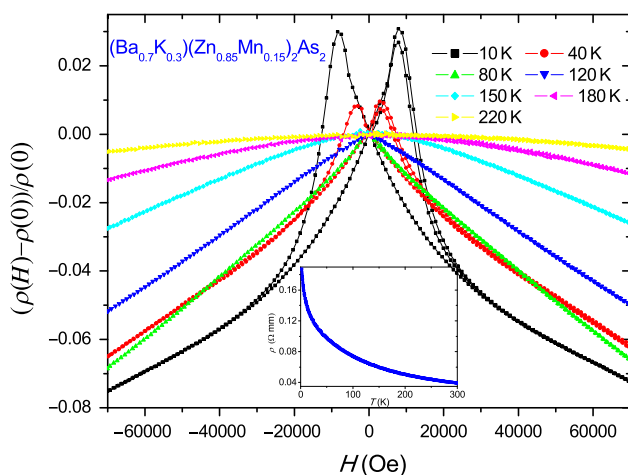


Fig. 3 Magnetoresistance curve measured in the external field up to $7T$ at $T = 10, 40, 80, 120, 150, 180,$ and 220 K, respectively, with obvious negative magnetoresistance below T_c . Inset: Resistivity curve of $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$

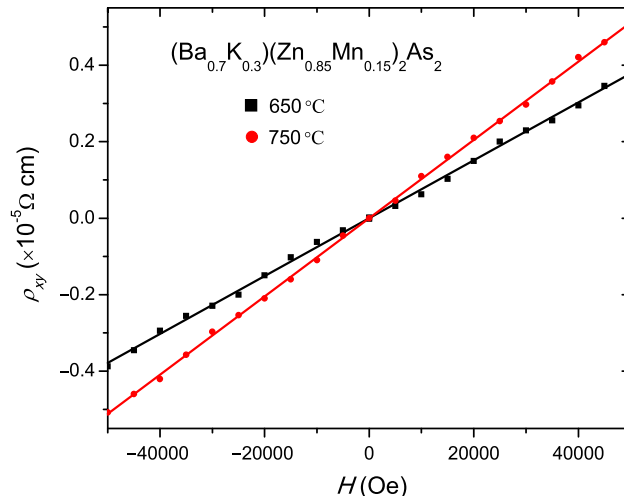


Fig. 4 Hall effect results at 250 K for $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ sintered at 650 and 750 °C, respectively, indicating the increased carrier density through reducing synthesis temperature

antiferromagnetic BaMn_2As_2 [16–18], and superconducting $(\text{Ba},\text{K})\text{Fe}_2\text{As}_2$ [7] all share the same crystal structure shown in Fig. 1, with quite good lattice matching in the a - b plane (mismatch $\leq 5\%$). These could provide distinct advantages in attempts to generate new functional devices based on junctions of various combinations of aforementioned DMS, superconductor, and magnetic states. The new DMS with decoupled spin charge doping mechanism [6, 8, 19–23] would be promising to develop brand new spintronics.

In summary, we successfully observed ferromagnetism at 230 K in the spin and charge decoupled diluted magnetic semiconductor $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$, with the tetragonal ThCr_2Si_2 -type structure identical to ferropnictide 122 superconductors. The relative high carrier density achieved by low temperature annealing results in high Curie temperature in $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$. With further enhanced carrier density, the Curie temperature of $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$ could probably even approach room temperature.

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