Chin. Sci. Bull. (2014) 59(21):2524–2527
DOI 10.1007/s11434-014-0398-z

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Letter

Condensed Matter Physics

# Ferromagnetism at 230 K in $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ diluted magnetic semiconductor

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Received: 29 November 2013 / Accepted: 19 December 2013 / Published online: 10 May 2014


**Abstract** We report the ferromagnetism with Cure temperature $T_c$ at 230 K in a new diluted magnetic semiconductor (DMS) $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ 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 $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ DMS, being different from (Ga,Mn)As where both spin & charge are induced simultaneously by heterovalence substation of $Mn^{2+}$ for $Ga^{3+}$. The $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ 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 (Ga,Mn)As, (In,Mn)As or (Ga,Mn)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 Li(Zn,Mn)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 $(Zn^{2+},Mn^{2+})$ substitutions, showing a Curie temperature up to $T_c = 50$ K. Comparing with classical DMS such as (Ga,Mn)As, the lower $T_c$ of the new "111" system is an obstacle for possible application. More recently, a new ferromagnetic DMS $(Ba,K)(Zn,Mn)_2As_2$ (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 (Ga,Mn)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 $(Ba,K)(Zn,Mn)_2As_2$ system as well. Here, we report ferromagnetism at 230 K in new diluted magnetic semiconductor $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$, with the Curie temperature higher than the record $T_c$ for (Ga,Mn)As [11].

Previous study shows that $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ demonstrates the highest $T_c$ for the $(Ba_{1-x}K_x)(Zn_{1-y}Mn_y)_2As_2$ system [8]. We hence choose $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ as the target composition in this study. Polycrystals of $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ 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 $(Ba,K)(Zn,Mn)_2As_2$. 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 °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 $2\theta$ range from 10° to 80°, the least-squares method was used to determine the lattice parameters with $a = 4.130$ Å and $c = 13.509$ Å, respectively.

Figure 2(a) shows temperature-dependent magnetization in zero-field-cooling (ZFC) and field cooling (FC) modes under 500 Oe for $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ 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 $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ at $T = 2$ K.

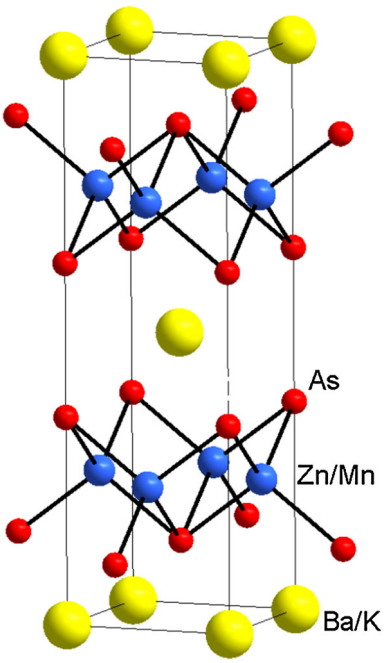


**Fig. 1** Crystal structure of $(Ba,K)(Zn,Mn)_2As_2$ identical to tetragonal $ThCr_2Si_2$, isostructural to "122" type iron pnictide superconductors

The saturation moment is $1\mu_B$ per Mn atom, comparable with that of (Ga,Mn)As [1], Li(Zn,Mn)As [6], and $(Ba,K)(Zn,Mn)_2As_2$ [8]. In Fig. 2(b) the spontaneous magnetization of $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ under 5 Oe in low temperature shows $T^{3/2}$ dependence expected for a homogeneous ferromagnet, as observed in (Ga,Mn)As [12].

As depicted in Fig. 3, the resistivity curve of $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$, similar to that of (Ga,Mn)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 (Ga,Mn)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 $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ 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 $T = 10$ 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 $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ sample sintered at 650 °C, the carrier concentration is about $8 \times 10^{20}$ $cm^{-3}$ as estimated from Hall measurement at 250 K that is enhanced a quarter than that of the sample sintered at 750 °C with $T_c$ 180 K [8] as shown in Fig. 4. It is argued that in low temperature annealed (Ga,Mn)As, the increase of carrier density probably accounts for the enhancement of Curie temperature [10–12]. Since potassium becomes melting at very low temperature (~63 °C) & boiling at 750 °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 $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$, 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 $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ synthesized at low temperature. We found that the sintering temperature at 650 °C is the threshold in our experiments in order to form the $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ structure.

In the present ''122'' DMS ferromagnet $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$, semiconducting $BaZn_2As_2$ [8],

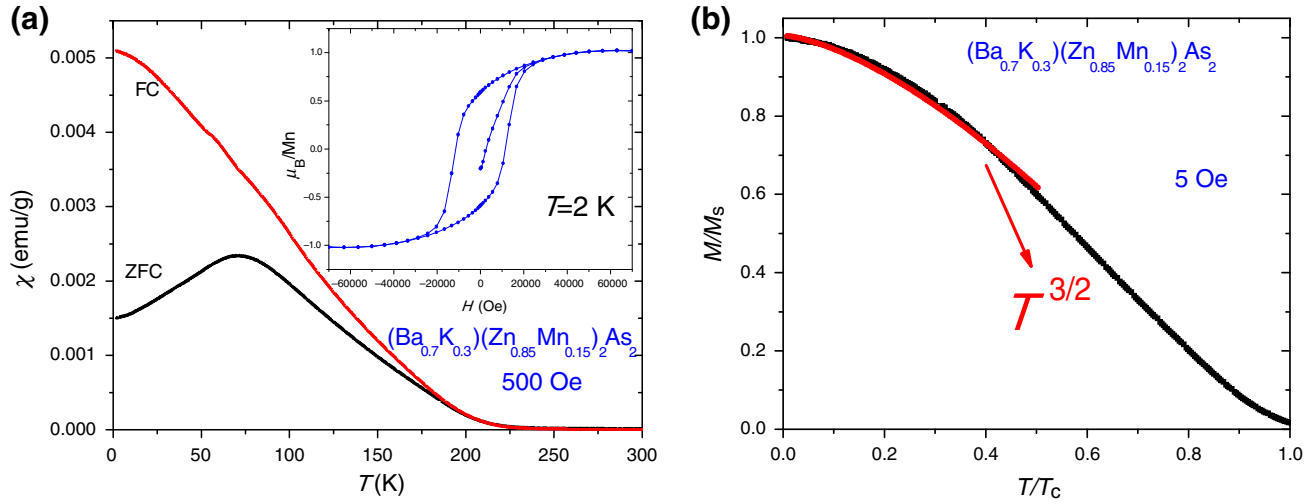


**Fig. 2** **a** magnetization measured in $H = 500$ G in $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ at both zero field cooling (ZFC)and field cooling (FC) modes, with Curie temperature ($T_c$) 230 K. Inset: The isothermal magnetic hysteresis curve $M(H)$, measured in the external field $H$ up to 7T; **b** the spontaneous magnetization curve under 5 Oe of $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$, showing $T^{3/2}$ dependence in low temperature expected for a homogeneous ferromagnet

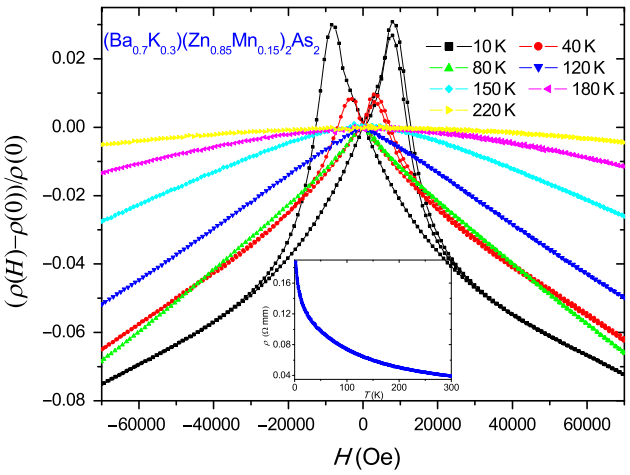


**Fig. 3** Magnetoresistance curve measured in the external field up to 7$T$ at $T = 10$, 40, 80, 120, 150, 180, and 220 K, respectively, with obvious negative magnetoresistance below $T_c$. Inset: Resistivity curve of $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$

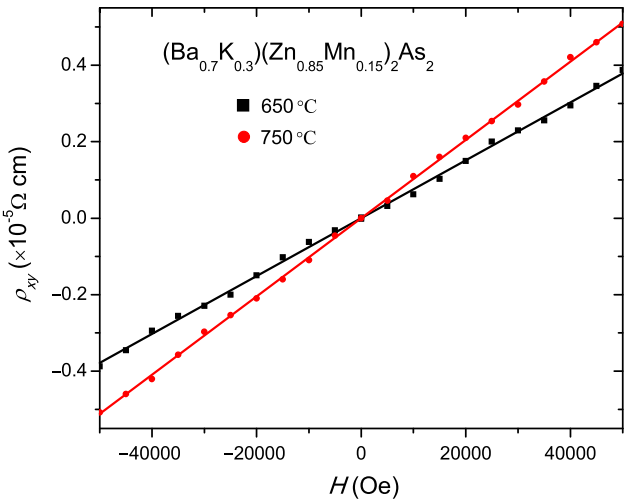


**Fig. 4** Hall effect results at 250 K for $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$ sintered at 650 and 750 °C, respectively, indicating the increased carrier density through reducing synthesis temperature

antiferromagnetic $BaMn_2As_2$ [16–18], and superconducting $(Ba,K)Fe_2As_2$ [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 $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$, 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 $(Ba_{0.7}K_{0.3})(Zn_{0.85}Mn_{0.15})_2As_2$. With further enhanced carrier density, the Curie temperature of $(Ba,K)(Zn,Mn)_2As_2$ could probably even approach room temperature.

**Acknowledgments** This work was supported by the National Natural Science Foundation of China and the Ministry of Science and Technology (MOST) of China. We are grateful to Prof. Uemura, Prof. F.L. Ning and Prof. Maekawa for helpful discussions.

## References

1. Ohno H (1998) Science 281:951–956
2. Dietl T (2010) Nat Mater 9:965–974
3. Zutic I, Fabian J, Das Sarma S (2004) Rev Mod Phys 76:323–410
4. Ohno H, Shen A, Matsukura F et al (1996) Appl Phys Lett 69:363–365
5. Dietl T, Ohno H, Matsukura F et al (2000) Science 587:1019–1022
6. Deng Z, Jin CQ, Liu QQ et al (2011) Nat Commun 2:422
7. Rotter M, Tegel M, Johrendt D (2008) Phys Rev Lett 101:107006
8. Zhao K, Deng Z, Wang XC et al (2013) Nat Commun 4:1442
9. Dunsiger SR, Carlo JP, Goko T et al (2010) Nat Mater 9:299–303
10. Ku KC, Potashnik SJ, Wang RF et al (2003) Appl Phys Lett 82:2302
11. Chen L, Yang X, Yang FH et al (2011) Nano Lett 11:2584
12. Macdonald AH, Schiffer P, Samarth N (2005) Nat Mater 4:195–202
13. Sasaki T, Sonoda S, Yamamoto Y et al (2002) J Appl Phys 91:7911–7913
14. Matsukura F, Ohno H, Shen A et al (1997) Phys Rev B 57:R2037
15. Dietl T (2008) J Phys Soc Jpn 77:031005
16. Singh Y, Ellern A, Johnston DC (2009) Phys Rev B 79:094519
17. Singh Y, Green MA, Huang Q et al (2009) Phys Rev B 80:100403
18. Panday A, Dhaka RS, Lamsal J et al (2012) Phys Rev Lett 108:087005
19. Deng Z, Zhao K, Gu B et al (2013) Phys Rev B 88:81203
20. Han W, Zhao K, Wang XC et al (2013) Sci China Phys Mech Astron 56:2026–2030
21. Ding C, Man HY, Qin C et al (2013) Phys Rev B 88:41102
22. Yang XJ, Li YK, Shen CY et al (2013) Appl Phys Lett 103:022410
23. Jin CQ, Wang XC, Liu QQ et al (2013) Sci China Phys Mech Astron 56:2337–2350