

Advances in new generation diluted magnetic semiconductors with independent spin and charge doping

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Abstract: As one branch of spintronics, diluted magnetic semiconductors (DMSs) are extensively investigated due to their fundamental significance and potential application in modern information society. The classical materials (Ga,Mn)As of III–V group based DMSs has been well studied for its high compatibility with the high-mobility semiconductor GaAs. But the Curie temperature in (Ga,Mn)As film is still far below room temperature because the spin & charge doping is bundled to the same element that makes the fabrication very difficult. Alternatively, the discovery of a new generation DMSs with independent spin and charge doping, such as (Ba,K)(Zn,Mn)₂As₂ (briefly named BZA), attracted considerable attention due to their unique advantages in physical properties and heterojunction fabrication. In this review we focus on this series of new DMSs including (I) materials in terms of three types of new DMSs, i.e. the “111”, “122” and “1111” system; (II) the physical properties of BZA; (III) single crystals & prototype device based on BZA. The prospective of new type of DMSs with independent spin and charge doping is briefly discussed.

Key words: diluted magnetic semiconductors; independent spin and charge doping; high Curie temperature

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1. Introduction

It is an everlasting dream to make electronic devices miniaturization, multi-functionalization, intellectualization, and low-power consumption in this current information society^[1]. But many bottleneck problems occur when the fabrication technology encounter nanometer scale^[2]. As one branch of spintronics, diluted magnetic semiconductors (DMSs) offers intriguing opportunities to combine semiconductor properties and ferromagnetism in a single material that would enable to fabricate new devices to process and store information simultaneously^[3,4].

DMSs researches date back to the concentrated magnetic semiconductors compounds, like EuX^[5] (X = O, S, Se and Te) & CdCr₂X₄^[6] (X = S and Se). However, the complicated growth and the relatively low Curie temperature (T_C) for these compounds limited these materials to fundamental studies. In 1980s, people payed much attention to Mn doped II–VI group DMSs, such as (Zn,Mn)Te, (Zn,Mn)Se, (Cd,Mn)Te, etc^[7] and Pb-SnMnTe^[8]. Yet T_C is still only several Kelvins due to lack of effective approach to dope carriers^[9]. Benefiting from the low temperature molecular beam epitaxy (LT-MBE) technique, Mn doped III–V group DMSs were explored in 1990s, like (Ga,Mn)As^[10–12] and (In,Mn)As^[13]. The highest T_C could reach 200 K in heavy Mn doped (Ga,Mn)As film with proper annealing procedure^[14–16].

It is of great fundamental significance and practical value to further improve T_C of (Ga,Mn)As^[17,18]. However, in (Ga,Mn)As, the Ga³⁺/Mn²⁺ substitution offers hole carriers and spins simultaneously, which make it difficult to individually con-

trol charge and spin concentrations and more importantly to improve T_C . Since 2011, a new type of DMSs with independent spin and charge doping, such as the “111” type Li(Zn,Mn)As^[19] and “122” type (Ba,K)(Zn,Mn)₂As₂ (BZA)^[20] named by its stoichiometry ratio, have been discovered. In these DMSs^[21], such as BZA, spins are introduced by isovalent Zn²⁺/Mn²⁺ doping, and charge carriers are introduced by heterovalent Ba²⁺/K¹⁺ substitution. Taking the advantage of freedom to individually control of charge and spin, BZA exhibit ferromagnetic order with T_C up to 230 K^[22] which is record of controlled reliable T_C among carrier mediated ferromagnetic DMSs^[16]. In this review, we demonstrate the discovery of three basic groups of new DMSs, namely the “111”, “122” and “1111” families (Fig. 1). Then we focus on physical properties of BZA and prototype device based on BZA single crystal. In the last section, we discuss the prospective of new type of DMSs with independent spin and charge doping.

2. Polycrystals synthesis and basic physical properties

2.1. “111” type DMSs

LiZnAs^[23,24] is a direct-gap semiconductor that has a cubic crystal structure with space group F-43m as shown in Figs. 1(a) & 1(b) and a band gap (1.61 eV) similar to that of GaAs^[25] (1.52 eV). Note that LiZnAs could be viewed as a zinc blende structure, in which Ga sites in (Ga,As) are replaced with Li and Zn. Benefitting on the LiFeAs^[26] iron superconductor fabrication experiences and facilities. Jin’s group firstly reported the successful synthesis of bulk form polycrystals Li(Zn,Mn)As^[19]. In principle, the Zn²⁺/Mn²⁺ replacement offers spins, and the off-stoichiometrical Li cation adjust the carrier’s type and concentration. But the long range ferromagnetic ordering was only observed with the excess Li doping and it is a

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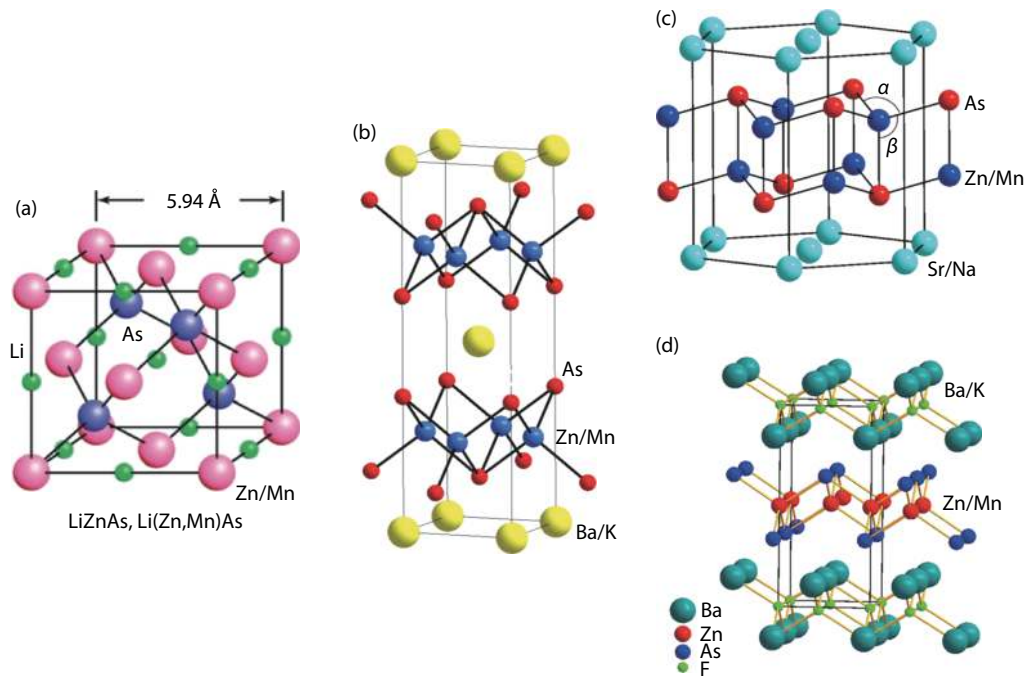


Fig. 1. (Color online) The crystal structure of (a) “111” Li(Zn,Mn)As with zinc blende structure, (b) “122” (Ba,K)(Zn,Mn)₂As₂ with ThCr₂Si₂ type structure, (c) (Sr,Na)(Zn,Mn)₂As₂ with CaAl₂Si₂ type structure, (d) “1111” (Ba,K)F(Zn,Mn)As with ZrCuSiAs structure. Adoped from Refs. [19, 20, 42, 47].

p-type rather than n-type as the theory prediction^[27]. The reason is that the excess Li¹⁺ prefers to occupy the Zn²⁺ sites based on a DFT calculation^[28]. The temperature dependence of M at 2 kOe (no difference between field cooling and zero field cooling procedures) was illustrated in Fig. 2(a), and external field H from 0 to 20 kOe dependence of M at 2 K is shown in Fig. 2(b). Clear signatures of ferromagnetic order were seen in these figures with the highest T_C of 50 K in Li_{1.1}(Zn_{0.85}Mn_{0.15})As sample. Semiconducting behavior of resistivity of LiZnAs (green line in Fig. 2(c)) changes to T -independent behavior for Li deficient systems, whereas much smaller resistivity and definite metallic behavior were found for Li excess samples. The resistivity increases monotonically with increasing Mn concentration in Fig. 2(d) which suggests that Mn acts as a scattering center. The onset of magnetic order reduces this scattering rate, as can be seen in the negative magnetoresistance of Li_{1.1}(Zn_{0.9}Mn_{0.1})As sample in Fig. 2(e) below T_C . Fig. 2(f) shows representative anomalous Hall effect of Li_{1.1}(Zn_{0.95}Mn_{0.05})As at 2 K, which exhibits p-type carriers with concentrations of $n \sim 10^{20} \text{ cm}^{-3}$.

In order to examine volume fraction and the ordered moment size, μ SR measurements were performed on sintered polycrystalline specimens of Li_{1.1}(Zn_{0.95}Mn_{0.05})As^[29]. The time spectra in zero field (ZF), shown in Fig. 3(a), clearly show an increase of the relaxation rate below ~ 25 K on Fig. 3(b), and measurements in longitudinal fields confirmed that the increase is from static magnetic order. This is in correspond with the earlier result in (Ga,Mn)As^[30]. The volume fraction of regions with static magnetism on Fig. 3(c) indicates a sharp transition at $T_C \sim 30$ K, and full volume magnetic order achieved when $T < 10$ K. Further studies on fabrication methods and heat treatments might help improve spatial homogeneity of the transition. The weak transverse field (WTF) of 30 Oe, shown in Fig. 3(d), also provide direct signal of the magnetic volume fraction^[31]. When the internal magnetic field is much larger than the applied external field, the scale of oscillation can reflect

the paramagnetic volume. The consistence of the ordered fraction from the measurements in ZF and WTF, shown in Fig. 3(c), supports the validity of our analysis of ZF- μ SR spectra.

The discovery of Li(Zn,Mn)As sparked extensive researches in this 111 type DMSs^[28, 32–36]. Fig. 4 shows only three of these new DMSs with independent spin and charge doping, e.g. Li(Zn,Mn)P, Li(Cd,Mn)P and Li(Zn,Co,Mn)As. Isostructural to Li(Zn,Mn)As^[19], Li(Zn,Mn)P^[28] is also a p-type DMSs with excess lithium providing charge doping. The highest T_C could reaches 34 K. The saturation moment per Mn (M_{sat}) is about $1\mu_B - 2\mu_B$, which is comparable to that in (Ga,Mn)As^[11], Li(Zn,Mn)As^[19], etc. $\rho(T)$ of Li(Zn,Mn)P decreases with increasing temperature, which shows semiconductor behaviors^[28]. Li(Zn,Mn)P is a soft magnetic material with about less than 100 Oe, shown in Fig. 4(a), based on the magnetic hysteresis loop and magnetoresistance curves. Magnetoresistivity $\rho_H(T)$ of Li_{1.04}(Zn_{0.9}Mn_{0.1})P at different external fields are shown in Fig. 4(b). $\rho_H(T)$ increases monotonically with decreasing temperature, showing a rapid rise below T_C . As shown in the inset of Fig. 4(b), the negative magnetoresistance is far from saturation in rather high magnetic field, in which spin orientation is fully aligned. In this condition, the negative magnetoresistance presumably results from the weak localization effects^[37]. Systematic μ SR measurements^[32] also confirmed that the magnetic volume fraction on Li_{1.15}(Zn_{0.9}Mn_{0.1})P could reaches nearly 100% at 2 K. Compared to Li(Zn,Mn)P, DMSs Li(Cd,Mn)P^[36] with optimum doping exhibits a higher T_C of 45 K as shown in Fig. 4(c). But more than 80% negative magnetoresistance, shown in Fig. 4(d), is a record in this 111 type DMSs. For this new type DMSs, spins and carries are indispensable.

Usually, the carriers are induced in Li site while spins in Zn site in all these above systems. Different from that idea, a new DMSs Li(Zn,Co,Mn)As^[33] was reported in which carriers and spins are both induced in Zn site simultaneously. Fig. 4(e) dis-

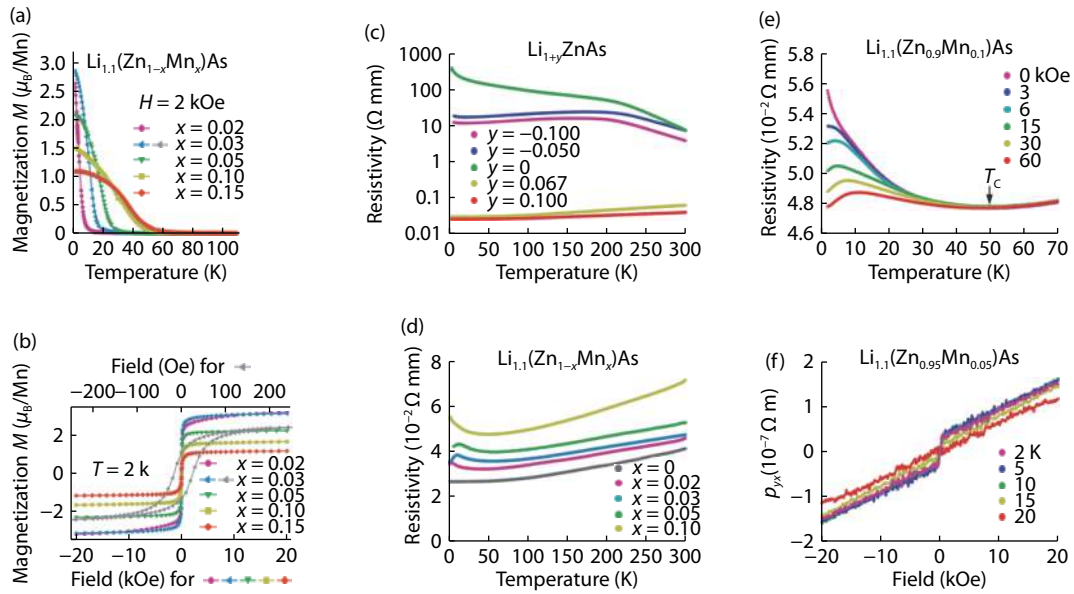


Fig. 2. (Color online) Magnetization & transport measurements of $\text{Li}(\text{Zn},\text{Mn})\text{As}$. (a) The temperature dependence of M in $H = 2$ kOe (no difference in FC and ZFC procedures). (b) M at 2 K in various values of external field H from 0 to 20 kOe. The grey symbols show a hysteresis loop in $x = 0.03$ system plotted for small field regions (top horizontal axis), which demonstrate a very small coercive field of 30–100 Oe. (c) Resistivity of $\text{Li}_{1+y}\text{ZnAs}$, showing metallic behavior of Li deficient ($y < 0$) and Li excess ($y > 0$) compounds. (d) Resistivity of $\text{Li}_{1.1}(\text{Zn}_{1-x}\text{Mn}_x)\text{As}$, showing the effect of increasing charge scattering with increasing Mn concentration x . (e) Resistivity of $\text{Li}_{1.1}(\text{Zn}_{0.9}\text{Mn}_{0.1})\text{As}$ in various external field H , which exhibits negative magnetoresistance below $T_C \sim 50$ K. (f) Hall resistivity of $\text{Li}_{1.1}(\text{Zn}_{0.95}\text{Mn}_{0.05})\text{As}$ at 2 K, which exhibits p-type carriers with concentrations of $n \sim 10^{20} \text{ cm}^{-3}$ together with the anomalous Hall effect due to spontaneous magnetization at $H = 0$. Adopted from Ref. [19].

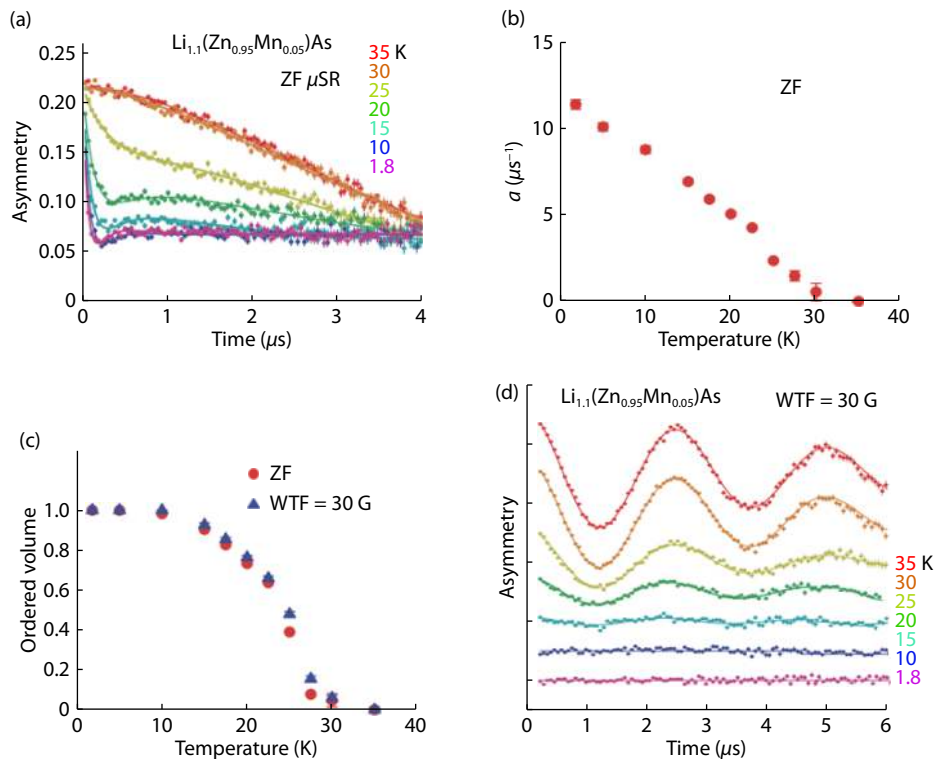


Fig. 3. (Color online) Results of μSR measurements in sintered polycrystalline specimens of $\text{Li}_{1.1}(\text{Zn}_{0.95}\text{Mn}_{0.05})\text{As}$. (a) Time spectra in zero field that exhibit onset of extra relaxation below $T \sim 30$ K. The solid lines represent fits to the relaxation function for dilute spin systems in zero field for the static case (often used for dilute alloy spin glasses), which exhibits a fast relaxation, plus a non-relaxing paramagnetic component. (b) The relaxation rate a of the signal that exhibits fast relaxation. (c) The volume fraction of the magnetically ordered region, derived from the amplitude of the fast relaxing signal. (d) μSR time spectra in the WTF of 30 Oe. The oscillation amplitude corresponds to the paramagnetic volume fraction. Adopted from Ref. [19].

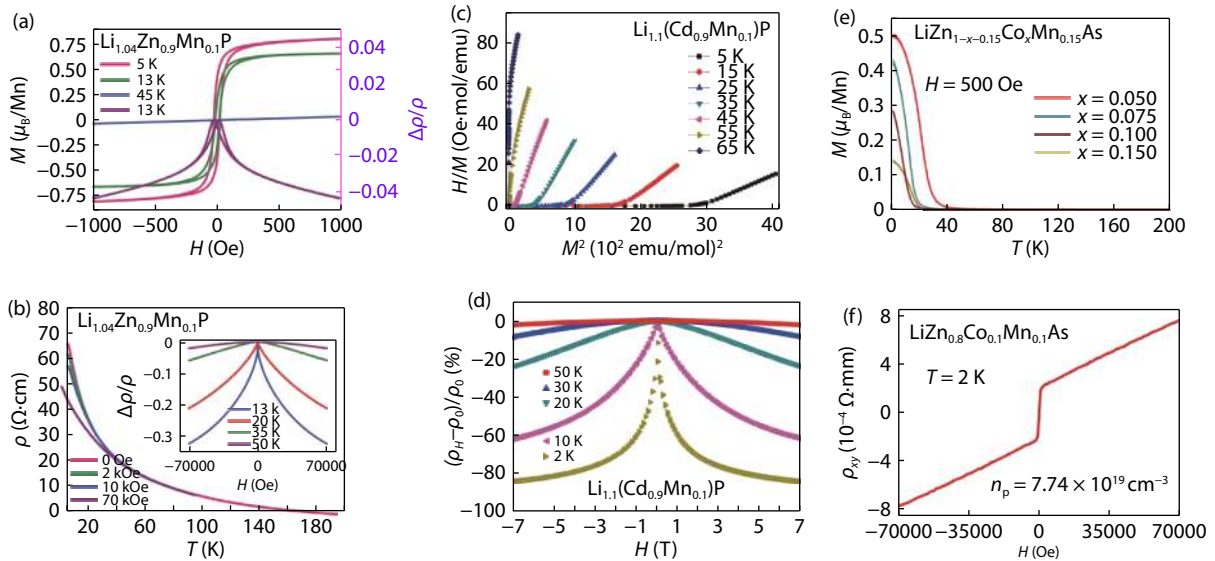


Fig. 4. (Color online) (a) $M(H)$ and $\rho(H)$ in $\text{Li}_{1.04}\text{Zn}_{0.9}\text{Mn}_{0.1}\text{P}$ show hysteresis, demonstrating ferromagnetism with small coercive field of about 50 Oe. (b) Magnetoresistivity $\rho_H(T)$ of $\text{Li}_{1.04}\text{Zn}_{0.9}\text{Mn}_{0.1}\text{P}$ at different external fields. Inset shows negative magnetoresistance at low temperature. (c) Arrott plots at various temperatures above and below T_C , shows the ferromagnetic transition temperature at 45 K. (d) Negative magnetoresistance at different temperatures. (e) The temperature dependence of M in $H = 100$ Oe for $\text{Li}(\text{Zn}_{1-x-0.15}\text{Co}_x\text{Mn}_{0.15})\text{P}$ (no difference in ZFC and FC procedures for small coercive fields). (f) Hall resistivity of $\text{Li}(\text{Zn}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{As}$ at 2 K, which exhibits p-type carriers with concentrations of $n \sim 7.74 \times 10^{19} \text{ cm}^{-3}$ together with the anomalous Hall effect due to spontaneous magnetization at $H = 0$. Adoped from Refs. [28, 33].

plays the temperature dependence of M in $H = 100$ Oe for $\text{Li}(\text{Zn}_{1-x-0.15}\text{Co}_x\text{Mn}_{0.15})\text{P}$. There is no difference in ZFC and FC procedures for small coercive fields with the highest T_C of 40 K in $\text{LiZn}_{0.80}\text{Co}_{0.05}\text{Mn}_{0.15}\text{P}$. The resistivity of $\text{Li}(\text{Zn}_{1-x-0.15}\text{Mn}_{0.15})\text{P}$ decreases with increase of Co doping. This means much more carriers are induced successfully. A field induced insulator-to-metal like transition around T_C can be observed with the external field of 1 T, which is due to the suppression of magnetic fluctuations below T_C . This feature is also observed in $\text{Li}(\text{Zn,Mn})\text{As}$ system^[19]. Fig. 4(d) demonstrates the Hall resistivity of $\text{Li}(\text{Zn}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{As}$ at 2 K, which exhibits p-type carriers with concentrations of $n \sim 7.74 \times 10^{19} \text{ cm}^{-3}$ together with the anomalous Hall effect due to spontaneous magnetization at $H = 0$.

2.2. "122" type DMSs

BaZn_2As_2 is a semiconductor synthesized at high temperature (>900 °C) with the tetragonal ThCr_2Si_2 crystal structure. A new type "122" DMSs $(\text{Ba,K})(\text{Zn,Mn})_2\text{As}_2$ has been synthesized with the $\text{Ba}^{2+}/\text{K}^{1+}$ substitution (hole carriers) and $\text{Zn}^{2+}/\text{Mn}^{2+}$ (spins) doping. Fig. 5(a) shows the temperature dependence of M in $H = 500$ Oe for $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ at ZFC and FC procedures with T_C 230 K. The hysteresis curves $M(H)$ are shown in the inset of Fig. 5(a). Fig. 5(b) exhibits 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, as expected for a homogeneous ferromagnet^[38]. Volume fraction of regions with static magnetic order, estimated by μSR measurements in ZF and WTF of 50 Oe are shown in Fig. 5(c). The μSR results indicate that static magnetic order develops in the entire volume with a sharp onset around T_C . Resistivity of $(\text{Ba}_{1-x}\text{K}_x)(\text{Zn}_{1-y}\text{Mn}_y)_2\text{As}_2$ for with several different charge doping levels are shown in Fig. 5(d). For BaZn_2As_2 semiconductor, doping K atoms into Ba sites introduces hole carriers, leading to metallic behavior in $(\text{Ba,K})\text{Zn}_2\text{As}_2$. The resistivity curves of $(\text{Ba}_{1-x}\text{K}_x)(\text{Zn}_{1-y}\text{Mn}_y)_2\text{As}_2$ for selected values of x up to

0.3, exhibit a small increase at low temperatures due to spin scattering effect caused by Mn dopants. This variation of resistivity is often observed in heavily doped semiconductors^[39]. Strictly metallic behavior (with monotonic decrease of resistivity with decreasing temperatures) is not a precondition of having a ferromagnetic coupling between Mn moments mediated by RKKY interaction^[12, 30]. Fig. 5(e) shows the magnetoresistance curve measured in the external field up to 7 T at different temperatures, showing obvious negative magnetoresistance below T_C . Fig. 5(f) shows the Hall effect results of $(\text{Ba}_{0.85}\text{K}_{0.15})(\text{Zn}_{0.90}\text{Mn}_{0.10})_2\text{As}_2$ at several temperatures with hole concentration about $4.3 \times 10^{20} \text{ cm}^{-3}$.

Different from $(\text{Ba,K})(\text{Zn,Mn})_2\text{As}_2$, another "122" type DMSs with hexagonal CaAl_2Si_2 was reported subsequently, such as $(\text{Ca,Na})(\text{Zn,Mn})_2\text{As}_2$ ^[40], $(\text{Sr,Na})(\text{Zn,Mn})_2\text{As}_2$ ^[41] and $(\text{Sr,Na})(\text{Cd,Mn})_2\text{As}_2$ ^[42], etc. Fig. 6(a) shows the temperature dependence of M in $H = 500$ Oe for $(\text{Ca}_{0.9}\text{Na}_{0.1})(\text{Zn,Mn})_2\text{As}_2$ with several different charge doping levels at ZFC and FC procedures. The highest T_C is 33 K. In Fig. 6(b), the temperature dependence of the volume fraction of regions with static magnetic order, derived from μSR measurements in ZF, is consistent with that of spontaneous magnetization under 5 Oe. The latter shows $T^{3/2}$ dependence in low temperature expected for a homogeneous ferromagnet^[22, 30, 38]. Due to the competition between nearest-neighbor antiferromagnetic interactions and ferromagnetic interactions from remote Mn moments, M_{sat} per Mn decreases with increasing Mn concentration. μSR results, shown in Fig. 6(d) are also consistent with the spontaneous magnetization under 10 Oe. This means $(\text{Sr}_{0.8}\text{Na}_{0.2})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ is also a homogeneous ferromagnet with almost 100% ordered volume fraction at low temperatures. Fig. 6(e) shows the temperature dependence of M in $H = 500$ Oe for $(\text{Sr}_{1-x}\text{Na}_x)(\text{Cd}_{1-x}\text{Mn}_x)_2\text{As}_2$ with several different charge doping levels x at ZFC and FC procedures with the highest T_C 13 K.

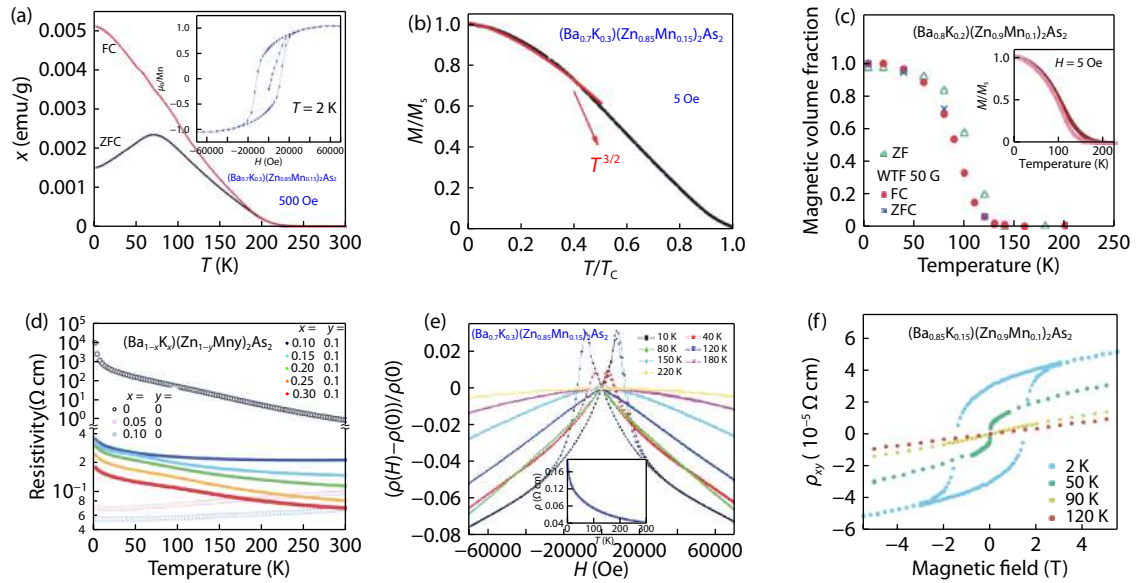


Fig. 5. (Color online) Magnetization & transport measurements of $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$. (a) The temperature dependence of M in $H = 500$ Oe for $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ at ZFC and FC procedures with T_C 230 K. Inset: The isothermal magnetic hysteresis curve $M(H)$, measured in the external field H up to 7 T. (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. (c) Volume fraction of regions with static magnetic order, estimated by μSR measurements in ZF and weak transverse field (WTF) of 50 G. No hysteresis is seen for WTF measurements with ZF cooling and field cooling in 500 G. Inset: DC magnetization results of the specimens used in μSR measurements. (d) Resistivity of $(\text{Ba}_{1-x}\text{K}_x)(\text{Zn}_{1-y}\text{Mn}_y)_2\text{As}_2$ for with several different charge doping levels. (e) Magnetoresistance curve measured in the external field up to 7 T at several selected temperatures, with obvious negative magnetoresistance below T_C . Inset: Resistivity curve of $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$. (f) Hall effect results from a sintered specimen of $(\text{Ba}_{0.85}\text{K}_{0.15})(\text{Zn}_{0.90}\text{Mn}_{0.10})_2\text{As}_2$ at several selected temperatures. A large coercive field is seen at 2 K. Adopted from Refs. [20, 22].

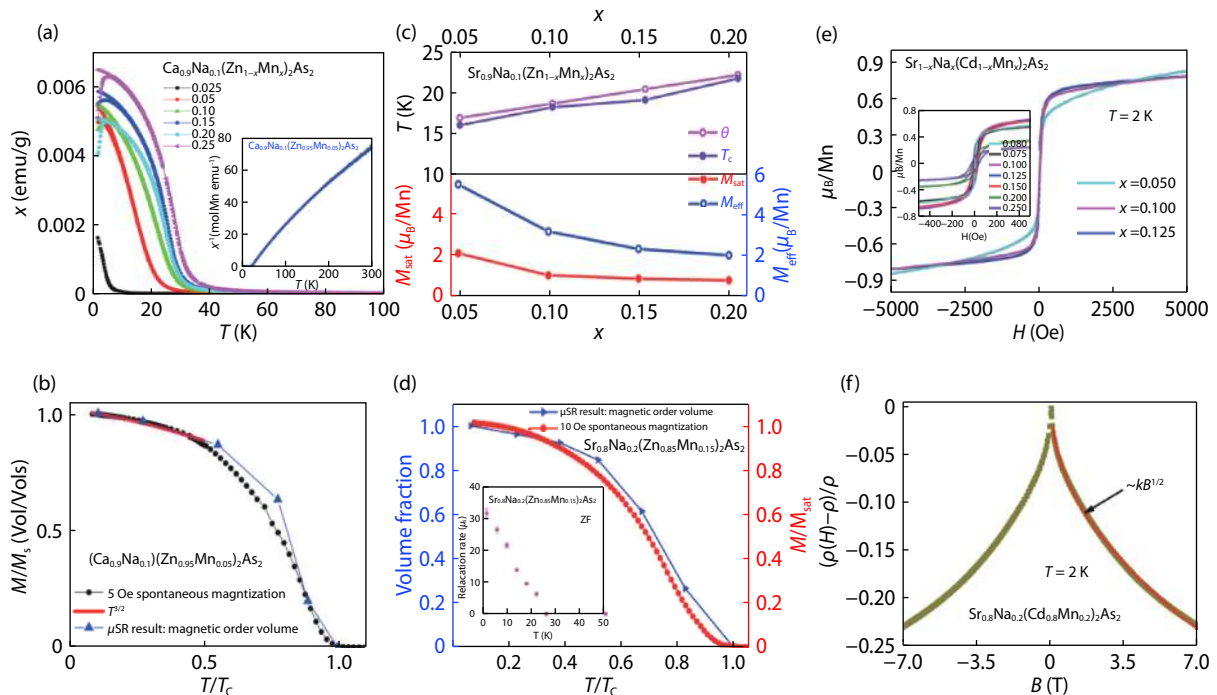


Fig. 6. (Color online) Magnetization & transport measurements of $(\text{Ca},\text{Na})(\text{Zn},\text{Mn})_2\text{As}_2$, $(\text{Sr},\text{Na})(\text{Zn},\text{Mn})_2\text{As}_2$ and $(\text{Sr},\text{Na})(\text{Cd},\text{Mn})_2\text{As}_2$. (a) The temperature dependence of M in $H = 500$ Oe for $(\text{Ca}_{0.9}\text{Na}_{0.1})(\text{Zn},\text{Mn})_2\text{As}_2$ with several different charge doping levels x at ZFC and FC procedures with the highest T_C 33 K. (b) The temperature dependence of the volume fraction of regions with static magnetic order, estimated by μSR measurements in ZF, consistent with that of spontaneous magnetization under 5 Oe, which shows $T^{3/2}$ dependence in low temperature expected for a homogeneous ferromagnet. (c) Curie temperature T_C , Weiss temperature θ , effective paramagnetic moment M_{eff} , and saturation moment M_{sat} for $(\text{Sr}_{0.9}\text{Na}_{0.1})(\text{Zn}_{1-x}\text{Mn}_x)_2\text{As}_2$ with different spin doping. (d) The temperature dependence of the volume fraction of regions with static magnetic order, estimated by μSR measurements in ZF, consistent with that of spontaneous magnetization under 10 Oe. Inset is the relaxation rate versus temperature, which is consistent with T_C . (e) The hysteresis curves of $(\text{Sr}_{1-x}\text{Na}_x)(\text{Cd}_{1-x}\text{Mn}_x)_2\text{As}_2$ samples with $x = 0.05, 0.1,$ and 0.125 , respectively, at 2 K. (f) Negative magnetoresistance of $(\text{Sr}_{0.8}\text{Na}_{0.2})(\text{Cd}_{0.8}\text{Mn}_{0.2})_2\text{As}_2$ at 2 K. Adopted from Refs. [40–42].

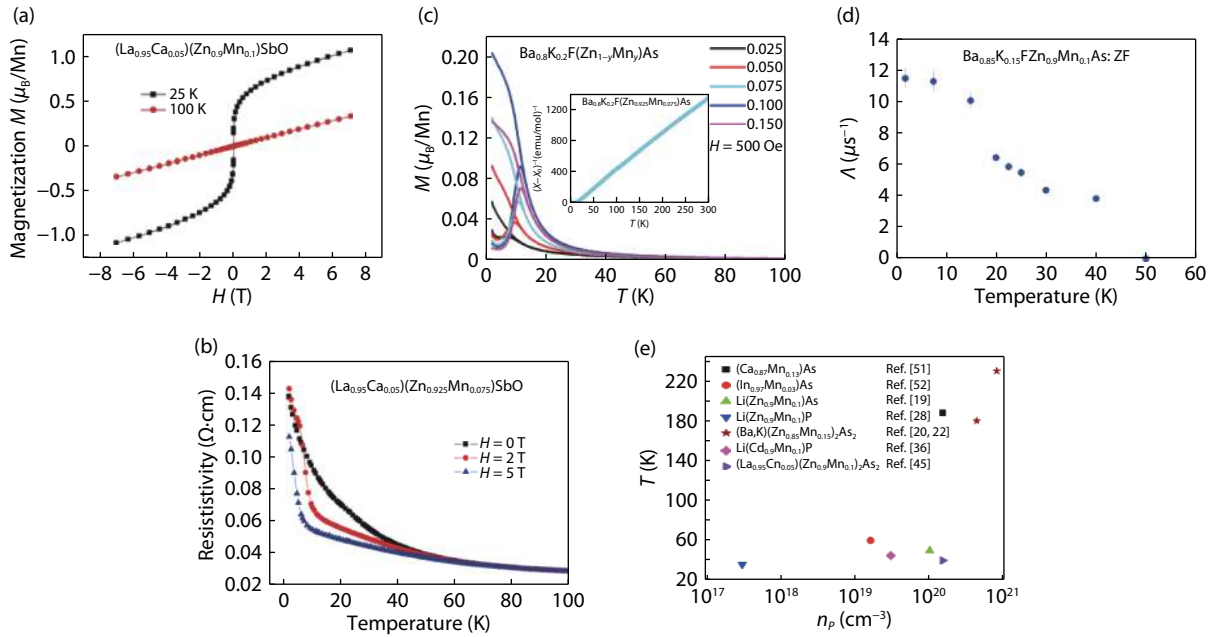


Fig. 7. (Color online) (a) Field dependences of magnetization for $(\text{La}_{0.95}\text{Ca}_{0.05})(\text{Zn}_{0.9}\text{Mn}_{0.1})\text{SbO}$ measured at 25 and 100 K. (b) resistivity of $(\text{La}_{0.95}\text{Ca}_{0.05})(\text{Zn}_{0.925}\text{Mn}_{0.075})\text{SbO}$ in various external field H , which exhibits negative magnetoresistance. (c) The temperature dependence of M in $H = 500$ Oe for $(\text{Ba}_{0.8}\text{K}_{0.2})\text{F}(\text{Zn}_{1-y}\text{Mn}_y)\text{As}$ with several different charge doping levels y at ZFC and FC procedures with the highest T_C 30 K. Inset shows the temperature dependence of the inverse susceptibility for $(\text{Ba}_{0.8}\text{K}_{0.2})\text{F}(\text{Zn}_{0.925}\text{Mn}_{0.075})\text{As}$. (d) The temperature dependence of fast relaxation rate Λ . The error bars represent the estimated standard deviations of the refined parameters. (e) Correlation between T_C and the hole concentration for several “111”, “122”, “1111” new types of diluted ferromagnetic semiconductors and typical III-V diluted ferromagnetic semiconductors. Adopted from Refs. [45, 47].

Magnetotransport measurements performed on $(\text{Sr}_{0.8}\text{Na}_{0.2})(\text{Zn}_{0.8}\text{Mn}_{0.2})_2\text{As}_2$ at 2 K under the field of up to 7 T are shown in Fig. 6(f). The negative magnetoresistance reached -23% at 2 K and 7 T. Taking the orbital effect into consideration, the negative magnetoresistance data are fit by $kB^{1/2}$ rule, indicating weak localization magnetoresistance at low temperature. The similar phenomenon is found in $(\text{Ga},\text{Mn})\text{As}$ system [37, 43].

2.3. “1111” type DMSs

Isostructural to the well-studied iron-based superconductor $\text{LaFeAs}(\text{O}_{1-x}\text{F}_x)$ [44], a new kind of “1111” DMSs were reported after the “111” and “122” DMSs, e.g. $(\text{La},\text{Ca})(\text{Zn},\text{Mn})\text{SbO}$ [45] and $(\text{Ba},\text{K})\text{F}(\text{Zn},\text{Mn})\text{As}$ [46, 47], etc. Fig. 7(a) shows the $M(H)$ for $(\text{La}_{0.95}\text{Ca}_{0.05})(\text{Zn}_{0.9}\text{Mn}_{0.1})\text{SbO}$ measured at 25 and 100 K, respectively. An abrupt increase of magnetization at 25 K suggests that a ferromagnetic state and paramagnetic state transition (T_C) occurs. The highest T_C reaches 40 K with proper doping in $(\text{La},\text{Ca})(\text{Zn},\text{Mn})\text{SbO}$ material. The resistivity increases monotonically with increasing Mn concentration, suggesting that scattering center of Mn. The resistivity of $(\text{La}_{0.95}\text{Ca}_{0.05})(\text{Zn}_{0.925}\text{Mn}_{0.075})\text{SbO}$ is shown in Fig. 7(b), with magnetic field up to 5 T. A negative magnetic resistance is clearly observed in a wide temperature region. This behavior can be well explained by the field suppression of the spin fluctuation [48]. Fig. 7(c) shows the $M(T)$ in ZFC and FC procedures under 500 Oe for the $(\text{Ba}_{0.8}\text{K}_{0.2})\text{F}(\text{Zn}_{1-y}\text{Mn}_y)\text{As}$ samples with $y = 0.025, 0.05, 0.075, 0.1$ and 0.15 , respectively. The highest T_C reaches 30 K for optimal Mn doping ($y = 0.1$). Above T_C , the susceptibility is fit to Curie-Weiss law as shown in the inset of Fig. 7(c), which indicates a ferromagnetic interaction between Mn^{2+} . The temperature dependence of the fast relaxation rate Λ is plotted in Fig. 7(d), exhibiting a monotonic increase with decreasing temperature

and reaching a maximum value at the lowest measurement temperature (2 K). The relationships between hole concentration and T_C of “111”, “122” and “1111” DMSs and other diluted ferromagnetic semiconductor systems are plotted in Fig. 7(e) [19, 20, 22, 28, 36, 45, 49, 50]. From $\text{Li}(\text{Zn},\text{Mn})\text{P}$ to $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$, T_C is considerably improved. As the Zener model predicted [51, 52], the ferromagnetic ordering in DMSs is mediated by hole carriers, and the Curie temperature is positive correlated with hole concentration.

3. Properties of $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$

3.1. X ray absorption spectroscopy (XAS) & angle-resolved photoemission spectroscopy (ARPES)

The origin of magnetic ordering on DMSs is still full of debates [53–56] meanwhile the general understanding for most common (III,Mn)V-based DMSs invokes As-derived valence-band states [57, 58] as mediators of ferromagnetic interactions. As for Mn-doped II–II–V semiconductors $(\text{Ba}_{1-x}\text{K}_x)(\text{Zn}_{1-y}\text{Mn}_y)_2\text{As}_2$, the details of the electronic structure and the role of As mediating (hole) states remain unresolved both in experiment and theory. A theory [59] predicts that the competition between the short-range antiferromagnetic (superexchange) interaction and the longer-range ferromagnetic interaction mediated by the itinerant holes determines the final ground state of BZA. Thus it is of great significance to verify the electronic states in $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$.

Fig. 8(a) exhibits the X-ray absorption spectroscopy (XAS) measurements [60] of the Mn $L_{2,3}$ edge on $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$. The line shapes of $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ are similar to $(\text{Ga}_{0.922}\text{Mn}_{0.078})\text{As}$ [61] and $(\text{Ga}_{0.958}\text{Mn}_{0.042}\text{N})$ [62], which indicates that the valence of

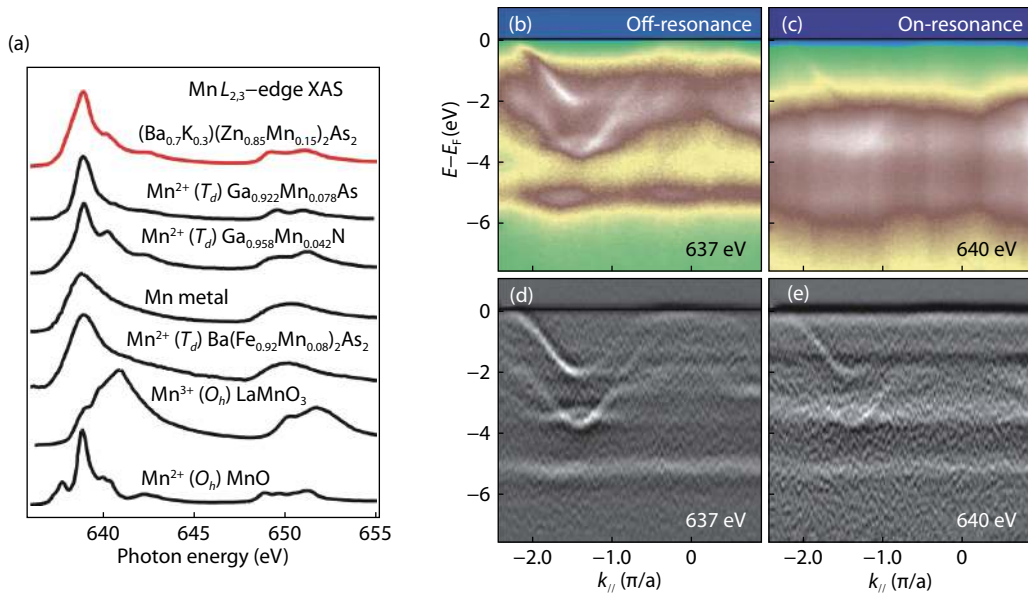


Fig. 8. (Color online) (a) Mn $L_{2,3}$ -edge XAS spectra of $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ polycrystal. The spectrum is compared with those of $(\text{Ga}_{0.922}\text{Mn}_{0.078})\text{As}$, $(\text{Ga}_{0.958}\text{Mn}_{0.042})\text{N}$, Mn metal, $\text{Ba}(\text{Fe}_{0.92}\text{Mn}_{0.08})_2\text{As}_2$, LaMnO_3 , and MnO . The valence and the local symmetry of the Mn atom are indicated for each compound. (b) & (c) ARPES energy-momentum intensity taken with on- and off-resonance energy photons. (d) & (e) Second derivatives of the on- and off-resonance ARPES spectra. Adoped from Refs. [60, 66].

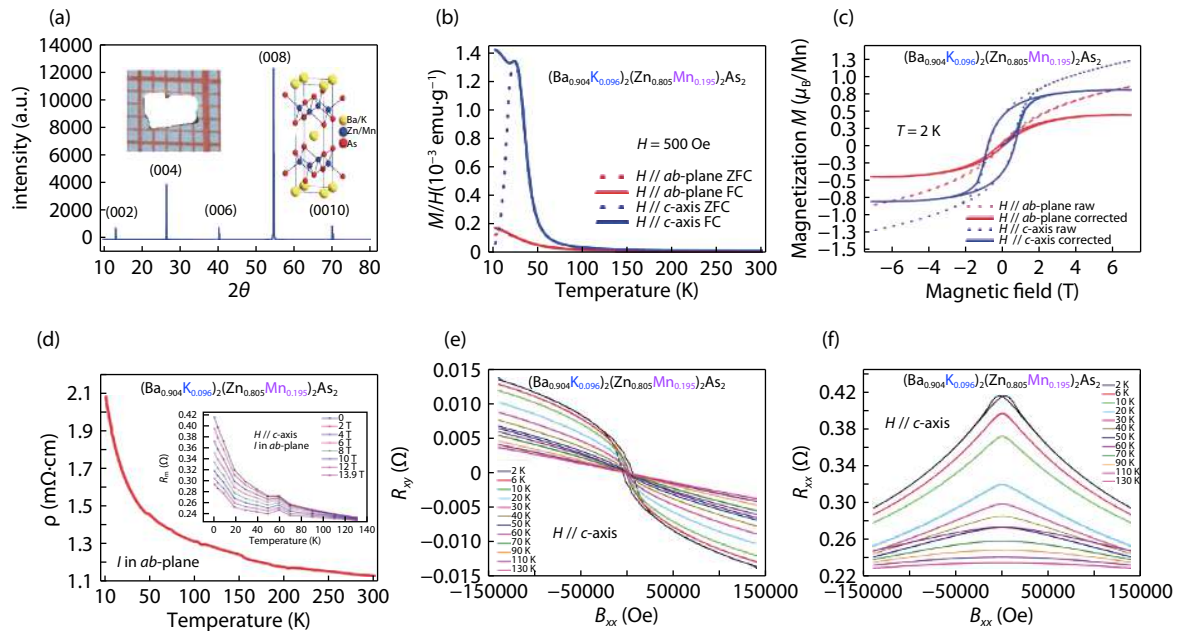


Fig. 9. (Color online) (a) The X-ray diffraction patterns of $(\text{Ba}_{0.904}\text{K}_{0.096})(\text{Zn}_{0.805}\text{Mn}_{0.195})_2\text{As}_2$ at room temperature. The inset shows the crystal structure (right) and its photograph (left). (b) The temperature dependence of M in $H = 500$ Oe for at ZFC and FC procedures in c -axis and ab -plane. (c) The hysteresis curves $M(H)$ measured at 2 K in different axis to exhibit magnetic anisotropy. (d) The temperature dependence of resistivity with current in ab -plane. Inset shows the MR(T) curves in various external field strengths. (e) & (f) The anomalous Hall effect R_{xy} and the magnetoresistance R_{xx} at several selected temperatures from 2 to 130 K. Adoped from Ref. [67].

Mn atoms is 2+ and that Mn 3d orbitals strongly hybridize with the As 4p orbitals as in $(\text{Ga},\text{Mn})\text{As}$ and $(\text{Ga},\text{Mn})\text{N}$ system. The strength of hybridization is weaker than $(\text{Ga},\text{Mn})\text{As}$ but stronger than $(\text{Ga},\text{Mn})\text{N}$ according to the shoulder structures around $h\nu = 640$ and 643 eV. The line shape shows a more localized nature than the Mn metal^[63] and metallic Mn doped into BaFe_2As_2 ^[64]. Different from LaMnO_3 and MnO ^[65], $(\text{Ba}_{0.7}\text{K}_{0.3})(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ does not show the clear multiple structures, consistent with the semi-metallic conductivity in $\text{Mn-BaZn}_2\text{As}_2$ ^[20]. Figs. 8(b)–(d) display the electronic structure

of $(\text{Ba}_{0.904}\text{K}_{0.096})(\text{Zn}_{0.805}\text{Mn}_{0.195})_2\text{As}_2$ by soft X rays angle-resolved photoemission spectroscopy (ARPES)^[66]. The results clarify the host valence-band electronic structure is primarily from the As 4p states. Two hole pockets around the Γ point explain the metallic behavior. The impurity band is well below the valence-band maximum (VBM), unlike that in $(\text{Ga},\text{Mn})\text{As}$, which is around the VBM. We conclude that the strong hybridization between the Mn 3d and the As 4p orbitals in $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$ plays a key role in creating the impurity band and inducing high temperature ferromagnetism.

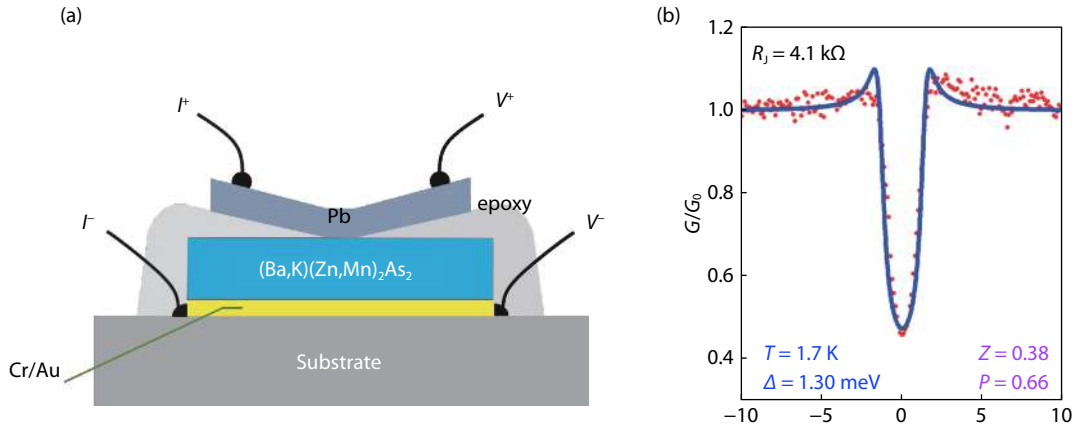


Fig. 10. (Color online) (a) Sketch of the $(\text{Ba}_{0.904}\text{K}_{0.096})(\text{Zn}_{0.805}\text{Mn}_{0.195})_2\text{As}_2/\text{Pb}$ junctions used for Andreev reflection spectroscopy. The inset is the normalization for the differential conductance G/G_0 . (b) Normalized differential conductance G/G_0 spectra (red dot) and their fits to the modified BTK theory (blue line) at selected temperatures at 1.7 K. Adapted from Ref. [67].

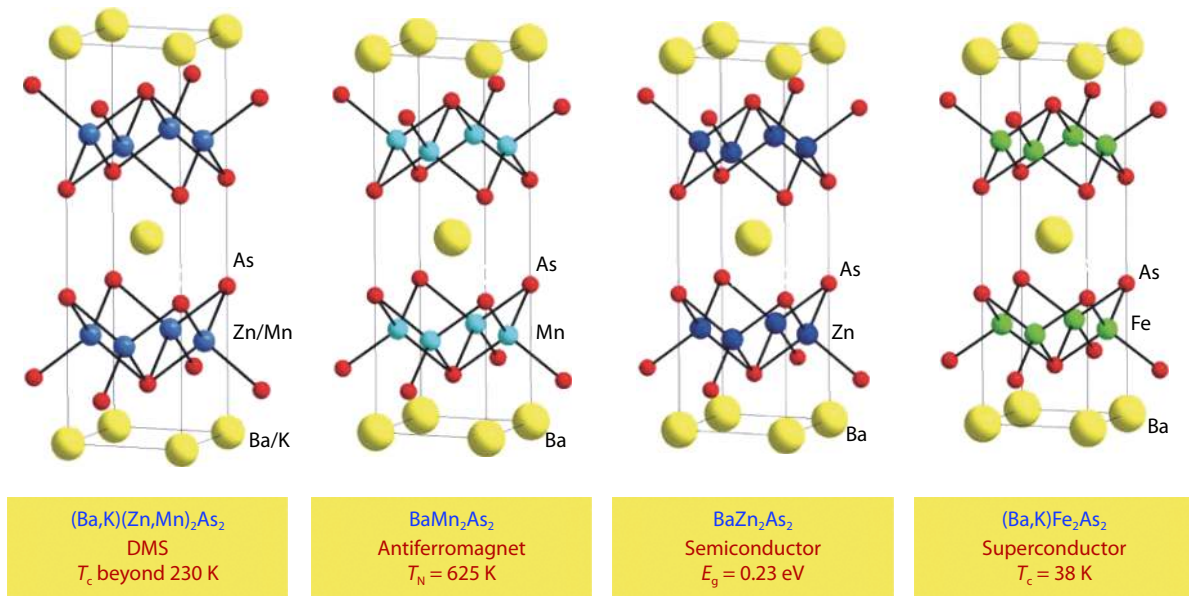


Fig. 11. (colour online) Crystal structures and key physical property of $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$, BaMn_2As_2 , BaZn_2As_2 and $(\text{Ba},\text{K})\text{Fe}_2\text{As}_2$.

3.2. Single crystal growth and spin polarization measurements

Compared with polycrystals, single crystals are ideal research platforms due to fewer defects. $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$ single crystal^[67, 68] is grown with flux method as shown in the inset of Fig. 9(a). Fig. 9(b) demonstrates the magnetization curves in different directions with T_c of about 50 K. Large anisotropic behavior is shown in Fig. 9(c) with easy axis along c . The semiconductor behavior on Fig. 9(d) arises from the localization effect^[69]. Based on the Magnetoresistance R_{xx} and Hall effect R_{xy} measurements, the hole carrier density increases from $2.82 \times 10^{20} \text{ cm}^{-3}$ at 2 K to $4.80 \times 10^{20} \text{ cm}^{-3}$ at 130 K. The increase is from the enhanced thermal excitation from the impurity band to the conduction band.

Andreev reflection spectroscopy (AR spectroscopy) is commonly used to achieve spin polarization (P) in various materials, e.g., $(\text{Ga},\text{Mn})\text{As}$ ^[70], $(\text{Ga},\text{Mn})\text{Sb}$ ^[71], $(\text{La},\text{Sr})\text{MnO}_3$ ^[72], CrO_2 ^[73], EuS ^[74], and HgCr_2Se_4 ^[75]. A schematic view of the BZA/Pb heterojunction is shown in Fig. 10(a). A “clean” interface, represented by the parameter Z , is a crucially required in spectral analysis.

For this experiment, the small Z value ($Z = 0.38 \ll 1$) implies the manifestation of a clean and transparent interface between BZA single crystal and Pb film. One key parameter for analysis is the differential conductance, $G(V) = dI(V)/dV$. It is measured as a function of dc-bias voltage (V) crossing the AR junction. Fig. 10(b) shows normalized differential conductance G/G_0 spectra (red dot) and their best fits to the modified Blonder–Tinkham–Klapwijk (BTK)^[76] theory (blue line) at 1.7 K. Spin polarization of 66% is obtained. Besides, about 40%–60% spin polarization is also achieved in a new DMSs $(\text{Ba},\text{Na})(\text{Zn},\text{Mn})_2\text{As}_2$ ^[77]. The success on AR junction paves a solid route to fabricate multilayer heterojunctions based on BZA.

Compared to classical DMSs, new type of DMSs has one great advantage, existence of numerous isostructural function materials. As shown in Fig. 11, $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$ shares the same tetragonal ThCr_2Si_2 type structure with semiconductor BaZn_2As_2 , antiferromagnetic BaMn_2As_2 ^[78] and superconductor $(\text{Ba},\text{K})\text{Fe}_2\text{As}_2$ ^[79]. The negligible mismatch of lattice constants in the a - b plane (less than 5%)^[20] makes the above materials promising to fabricate multilayer functional heterojunctions. These heterojunctions should have near perfect inter-

Table 1. Some selected properties in new diluted magnetic semiconductors with independent spin & charge doping, superconductors and anti-ferromagnets.

Diluted magnetic semiconductors (Highest Curie temperature T_C)				Superconductors (Superconducting temperature T_C')		Antiferromagnets (Neel's temperature T_N)		
Type	Structure	Material	T_C (K)	Material	T_C' (K)	Material	T_N (K)	
"111"	Zinc blende type structure (F-43m)	Li(Zn,Mn)As ^[19]	50	LiFeAs ^[26] (P4/nmm)	18	LiMnAs ^[82] (P4/nmm)	378.3	
		Li(Zn,Mn)P ^[28, 32]	34					
		Li(Cd,Mn)P ^[36]	45					
		Li(Zn,Co,Mn)As ^[33]	40					
		Li(Zn,Cu,Mn)As ^[34]	33					
"122"	Tetragonal ThCr ₂ Si ₂ type structure (P4/nmm)	(Ba,K)(Zn,Mn) ₂ As ₂ ^[20, 22, 60, 64, 84–88]	230	(Ba,K)Fe ₂ As ₂ ^[79] (P4/nmm)	38	BaMn ₂ As ₂ ^[78] (P4/nmm)	625	
		(Ba,K)(Zn,Mn) ₂ P ₂ ^[89]	Theory					
		Mn-doped BaZn ₂ Sb ₂ ^[90]						
		(Ba,K)(Zn,Mn) ₂ (As,Pn) ₂ (Pn = P, Sb) ^[83]	185					
		(Ba,Na)(Zn,Mn) ₂ As ₂ ^[77]	20					
		Ba(Zn _{1-2x} Mn _x Cu _x) ₂ As ₂ ^[91]	44					
		(Ba,K)(Cu,Mn) ₂ Se ₂ ^[92]	18					
		Ba(Zn,Co) ₂ As ₂ ^[80]	45					
		Hexagonal CaAl ₂ Si ₂ type structure (P-3m1)	(Ca,Na)(Zn,Mn) ₂ As ₂ ^[40]					33
			(Sr,Na)(Zn,Mn) ₂ As ₂ ^[42]					24
			(Sr,Na)(Cd,Mn) ₂ As ₂ ^[41]					13
			(Sr,K)(Zn,Mn) ₂ As ₂ ^[93, 94]					12
			(Ba,K)(Cd,Mn) ₂ As ₂ ^[95]					16
"1111"	ZrCuSiAs type structure (P4/nmm)	(La,Ca)(Zn,Mn)SbO ^[45]	40	LaFeAs(O,F) ^[44] (P4/nmm)	26	LaMnAsO ^[96] (P4/nmm)	317	
		(La,Ca)(Zn,Mn)AsO ^[45, 97]	30					
		(La,Ba)(Zn,Mn)AsO ^[98, 99]	40					
		La(Zn,Mn)AsO ^[100]	Theory					
		(La,Sr)(Cu,Mn)SO ^[101]	200					
		(La,Sr)(Zn,TM)AsO ^[101, 102] (TM = Mn, Fe, Co)	30					
		(Ba,K)F(Zn,Mn)As ^[47]	30					
		La(Zn,Mn,Cu)SbO ^[103]	15					
		La(Zn,Mn,Cu)AsO ^[104]	8					
		SrF(Zn,Mn,Cu)Sb ^[105]	40					

face that enable deep insight of many new physical phenomena and physical rules. Recently, a series of single-phased, single-oriented thin (Ba,K)(Zn,Mn)₂As₂ films are successfully fabricated by pulsed laser deposition (PLD) on different substrates, e.g. LSAT, SrTiO₃, LaAlO₃, Si and MgAl₂O₄. A n-type polycrystalline BZA DMSs Ba(Zn,Co)₂As₂^[80] was reported recently. All these results offers much research room for many kinds of heterojunctions in the future^[4].

4. Summary and outlook

There are three main group of new diluted magnetic semiconductors with independent charge and spin doping, i.e. the "111", "122" and "1111" type, as listed in Table 1. BZA is unique in that it has T_C above 200 K. Note that there are other four DMSs which are isostructural to BZA but have low T_C . What makes BZA so special is one open question. The accurate answer to the question could be the clue to seek mechanism of DMSs and the guiding light to search for room temperature ferromagnetic DMSs.

Taking the advantage of lattice matched superconductors, semiconductors and antiferromagnetic compounds, these new types of DMSs have potential to fabricate multilayer heterojunctions^[3, 4]. In the roadmap^[81] for spintronic materials, BZA is proposed as one of the most promising DMSs materials. Two

major research fields are recommended for future studies of BZA: (I) to search for Curie temperature higher than room temperature based on the enhancing ferromagnetism interactions; (II) to fabricated isostructural DMSs junctions with various lattice matched materials.

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