(Sr1-xNax)(Cd1-xMnx)2As2: A new charge and spin doping decoupled diluted magnetic semiconductors with CaAl2Si2-type structure

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I. INTRODUCTION

The successful discovery of carrier-induced ferromagnetism in thin-film form via the molecular beam epitaxy of III–V compound semiconductor compounds has promoted considerable research interest in diluted magnetic semiconductors (DMSs), thus realizing the fabrication of quantum structures combined with electron spins, which exhibit outstanding properties and functionalities.1–7 The ferromagnetic Curie Temperature \( T_C \) exceeding 200 K has been realized in (Ga,Mn)As systems with a relatively high hole density of doping Mn (~12% Mn doping in GaAs).8,9 Reaching \( T_C \) at room temperature is believed to be possible if greater concentrations of holes and magnetic ions can be achieved in the materials.9 Nevertheless, in III–V DMSs like (Ga,Mn)As systems with off-stoichiometry of Li concentrations to dope hole carriers and (Zn,Mn) substitution to supply magnetic moments, this system exhibited ferromagnetic order with \( T_C \) up to 50 K.10 Shortly after, another new DMS, (Ba,K)(Zn,Mn)\(_2\)As\(_2\), with a relatively high \( T_C \) (up to 230 K) has been reported.11,12 These new bulk DMSs, which are available for performing muon spin relaxation (\( \mu \)SR), nuclear magnetic resonance (NMR), angle-resolved photoemission spectroscopy (ARPES), and neutron scattering, opened up a window to investigate the individual influence of carriers and local moments on ferromagnetism.10,21,22 ARPES, as well as theoretical studies, has shown that Mn 3d and As 4p orbitals play important roles in inducing high-temperature ferromagnetism, and hole doping drives the ferromagnetism effect in (Ba,K)(Zn,Mn)\(_2\)As\(_2\) system.21,23 Previous \( \mu \)SR measurements reported that the ferromagnetism in \( \text{Li}(\text{Zn,Mn})\text{As} \), \( \text{(Ba,K)}(\text{Zn,Mn})\text{As}_2 \), \( (\text{La,R})\text{O}(\text{Zn,Mn})\text{As} \) \( (R = \text{Ba, Ca}) \),15,24 and \( \text{Li}(\text{Zn,Mn})\text{P} \) \( \text{shares the same ferromagnetic mechanism of the ferromagnetic order with (Ga,Mn)As. However, the \( \mu \)SR measurements performed on (Sr,Na)(Zn,Mn)\(_2\)As\(_2\) with hexagonal CaAl\(_2\)Si\(_2\)type structure interestingly exhibited different exchange interactions of Mn atoms.} \)14

In this article, we report a new Mn-doped cadmium-based ferromagnetic semiconductor \((\text{Sr}_{1-x}\text{Na}_x)(\text{Cd}_{1-x}\text{Mn}_x)\text{As}_2\) with decoupled spin and charge doping, which shares the same structure as that of the “122” \((\text{Sr,Na})(\text{Zn,Mn})\text{As}_2\) DMS with the hexagonal CaAl\(_2\)Si\(_2\) structure (Figs. 1(a) and 1(b)). The \text{Cd}_2\text{As}_2 layers form a honeycomb-like network which has attracted much attention in the recently essential and extensive investigation of topological insulators.25,26 Up until now, studies on the physical properties of parent compound \( \text{SrCd}_2\text{As}_2 \) have not been reported yet. Here, we determined the bandgap of \( \text{SrCd}_2\text{As}_2 \) from the carrier transport properties and obtained the reliable electronic structure through first-principles calculations which provided good agreement with the experimental bandgap. 15% Na and Mn co-doping in \( \text{SrCd}_2\text{As}_2 \) resulted in a ferromagnetic transition below \( T_C \) of ~13 K and a relatively small coercive field below ~24 Oe, which are possibly advantageous for spin flip manipulation.

II. EXPERIMENTS

Polycrystalline \((\text{Sr}_{1-x}\text{Na}_x)(\text{Cd}_{1-x}\text{Mn}_x)\text{As}_2\) was synthesized through solid state reaction by sintering a mixture of intermediate products \( \text{Na}_3\text{As}, \text{SrAs}, \) pure Cd, Mn, and As powders in a silica tube filled with Ar gas at 700 °C for 20 h, a
procedure similar to what was employed for (Sr,Na) (Zn,Mn)2As2.14 The crystal structure, phase purity, and lattice constants of the resulting powders were examined using power X-ray diffraction (XRD; Philips X’pert diffractometer) with Cu-Kα radiation at room temperature and with the aid of Rietveld refinement using the GSAS software package.27 The first-principle electronic structure calculations were performed using experimental crystallographic parameters and the full-potential linearized augmented plane wave (LAPW) method using the WIEN2k package.28 The general gradient approximation (GGA) was used for calculating the exchange-correlation potential.29 The energy cut-off was set to R<sub>mingmax</sub> = 8.0, and the k-point sample was set to 31 × 31 × 16. The DC magnetic susceptibility measurements were performed with a superconducting quantum interference device (SQUID-VSM; Quantum Design) at temperatures ranging from 2 to 300 K. The electric transport was measured with a four-probe technique using silver paste electrodes on a Quantum Design PPMS in the same temperature ranges.

III. RESULTS AND DISCUSSION

Figure 1(c) shows the X-ray diffraction results of (Sr<sub>x</sub>Na<sub>1-x</sub>)(Cd<sub>y</sub>Mn<sub>1-y</sub>)2As2 for x = 0, 0.05, 0.075, 0.1, 0.125, and 0.15, respectively. All the Bragg peaks can be indexed into the same structure of the undoped compound SrCd2As2, which has a layered crystal structure belonging to the hexagonal CaAl2Si2-type structure with the space group P-3m1 (No.164), as shown in Figs. 1(a) and 1(b). In the structure of SrCd2As2, the Sr atoms occupied the one-fold Wyckoff position 1a (0 0 0), and the Cd and As atoms orderly occupied the two-fold sites in Wyckoff position 2d (1/3 1/3 0). (Sr,Na)(Cd,Mn)2As2 showed a layered structure and shared the (Cd,Mn)-centered [Cd,Mn]As₆ tetrahedral coordination and the (Sr,Na)-centered [Sr,Na]As₆ octahedral coordination, which differ from the previously reported structure of “122” ferromagnetic DMS (Ba,K)(Zn,Mn)₂As₂.11,20 The lattice parameters of all polycrystalline samples were calculated using the X-ray diffraction data through the GSAS software package,27 as shown in Fig. 1(d). The calculated lattice parameters of SrCd₂As₂ were a = 4.4517 Å and c = 7.4252 Å, which are consistent with the previously reported values of a = 4.4521 Å and c = 7.4161 Å, respectively.30 Compared with the lattice parameters of parent compound SrCd₂As₂, the a-axis and c-axis shrunk monotonically with the increasing Na and Mn doping of (Sr<sub>1-x</sub>Na<sub>x</sub>)(Cd<sub>1-y</sub>Mn<sub>y</sub>)₂As₂ following the Vegard’s law. These results indicate the successful chemical doping of Na and Mn.

DC-magnetization measurements were performed on all specimens. Ferromagnetic transition was only observed in compounds with co-doping during carrier doping via (Sr,Na) substitution and spin doping through (Cd,Mn) substitution, which means that the hole-type carriers introduced by Na doping is crucial in the formation of ferromagnetic ordering.21,23 Fig. 2(a) shows the measurements of magnetic susceptibility for the (Sr<sub>1-x</sub>Na<sub>x</sub>)(Cd<sub>1-y</sub>Mn<sub>y</sub>)₂As₂ samples under field H = 500 Oe with x = 0.05, 0.075, 0.1, 0.125, 0.15, 0.2, and 0.25, respectively. No obvious difference was observed between the field cooling (FC) and zero-field cooling (ZFC) procedures. Clear signatures of ferromagnetic order are observed in the curves. The maximum T<sub>C</sub> for optimal Na and Mn doping (x = 0.15) is 13 K. T<sub>C</sub> was monotonically suppressed with further Na or Mn doping.

The hysteresis curves of (Sr<sub>1-x</sub>Na<sub>x</sub>)(Cd<sub>1-y</sub>Mn<sub>y</sub>)₂As₂ samples with x = 0.05, 0.1, and 0.125, respectively, at T = 2 K is shown in Fig. 2(b). The saturation moment (M<sub>sat</sub>) is 0.81 μB/Mn for x = 0.1, which is comparable to that of (Sr<sub>0.9</sub>Na<sub>0.1</sub>)(Zn<sub>0.1</sub>Mn<sub>0.9</sub>)₂As₂,14 Inset in Fig. 2(b) exhibits the hysteresis loops for the corresponding samples in Fig. 2(a), which are plotted in small field regions. Small coercive field (H<sub>C</sub>) was observed in this system (less than 24 Oe), which is even smaller than that of Li(Mn,Zn)As (30–100 Oe). The material with very small H<sub>C</sub>, as a soft material, may be more conducive to spin manipulations in the future. The M<sub>sat</sub> of the samples decreased from 0.83 to 0.29 μB/Mn with increasing Na and Mn doping.
Mn doping, whereas the $H_C$ increased from 5 to 24 Oe. These changing trends in the suppression of $T_C$ and saturation moments with higher Mn doping levels much likely arose from the competition between the antiferromagnetic interaction of Mn moments occupying the nearest neighbor position of Zn and ferromagnetic interactions regulated by the hole carrier of distant Mn moments, i.e., the Rudermann–Kittel–Kasuya–Yosida (RKKY)-like interaction. Similar changing trends were found in other magnetic ions-doped systems.\textsuperscript{4,10,14,16}

The results of electronic transport studies are shown in Fig. 3. Fig. 3(a) shows the electrical resistivity, $\rho$, versus temperature, $T$, for $(\text{Sr}_{1-x}\text{Na}_x)\text{Cd}_2\text{As}_2$ with $x = 0, 0.03, \text{and } 0.05$, respectively. For the sample with $x = 0$, the resistance was out of the measuring range below 110 K. Resistivity measurements indicate that SrCd\textsubscript{2}As\textsubscript{2} is a semiconductor with thermal activation energy, $E_a = 0.108 \text{ eV}$, i.e., $E_g = 2E_a = 0.21 \text{ eV}$. As shown in Fig. 3(b), the value of $E_a$ was obtained by fitting the thermal activation formula

$$
\rho(T) = \rho_0 \exp\left( \frac{E_a}{k_B T} \right),
$$

where $\rho_0$ is a constant, and $k_B$ is the Boltzmann constant, at temperatures of 110 to 300 K. Doping Na atoms into Sr sites introduced hole carriers, leading to the significant decrease in resistivity by approximately four orders in $(\text{Sr},\text{Na})\text{Cd}_2\text{As}_2$.

To better understand the structure and bonding, as well as the observed relatively wide band gap semiconducting properties, first principles calculations were performed on the structure of SrCd\textsubscript{2}As\textsubscript{2}. The computed band structures are...
shown in Fig. 3(c). SrCd\textsubscript{2}As\textsubscript{2} is a direct narrow gap semiconductor with separation between the top of the valence band and the bottom of the conduction band of \(\sim 0.2\) eV, which coincides with the transport measurements discussed above.

Figure 3(d) shows the temperature dependence of \(\rho\) for \((\text{Sr}_{1-x}\text{Na}_{x})(\text{Cd}_{1-y}\text{Mn}_{y})\text{As}_2\) on several doping levels of \(x\), where \(x = 0.03, 0.05, 0.075, 0.1, 0.125, 0.15, 0.2,\) and 0.25, respectively. The resistivity increased monotonically with increasing Na and Mn concentrations. For low Mn-doped samples \((x = 0.03, 0.05)\), metallic-like conduction behavior was observed at high temperatures, whereas clear upturns in resistivity at low temperatures became more remarkable with the increase in the Mn doping level. The increase in resistivity was probably due to the spin scattering of carriers caused by Mn dopants. The partial substitution of strontium by sodium and of zinc by manganese induces a semimetal to insulator-like transition within the \((\text{Sr}_{1-x}\text{Na}_{x})(\text{Cd}_{1-y}\text{Mn}_{y})\text{As}_2\) series, due to the interaction of the local spins and conduction electrons. This anomalous behavior in resistivity was observed in other DMSs,\(^{11,34}\) such as \((\text{Ba,K})(\text{Zn,Mn})_2\text{As}_2\)\(^{11}\) system and \((\text{Ga,Mn})\text{N}\)\(^{32}\) system.

Magnetotransport measurements performed on \((\text{Sr}_{0.8}\text{Na}_{0.2})(\text{Cd}_{0.8}\text{Mn}_{0.2})\text{As}_2\) at \(T = 2\) K under the field of up to 7 T are shown in Fig. 4(a). The negative magnetoresistance (defined as \([\rho(H) - \rho(0)]/\rho(0)\)) reached up to \(-23\%\) at \(T = 2\) K and \(H = 7\) T, in which spin orientation was fully aligned according to the isostructural magnetization data shown in Fig. 2(b); however, magnetization was still far from saturation. Taking the orbital effect into consideration, the negative magnetoresistance data at \(T = 2\) K can be described by the equation\(^{33}\)

\[
\frac{\Delta \rho}{\rho} = k B^{1/2},
\]

where \(k = n_v e^2 C_0 \hbar e^2 / (2 \pi^2 \hbar^3)\), \(C_0 \approx 0.605\), \(e\) is the elemental charge, \(\hbar\) is the reduced Planck constant, and \(1/2 \leq n_v \leq 2\) depending on the number of hole sub-bands contributing to the charge transport. A best fit to Equation (2) gives \(n_v = 0.64\) (the red line in Figure 4(a)), which indicates that weak localization magnetoresistance appeared at low temperatures.\(^{33}\) A similar phenomenon was found in the \((\text{Ga,Mn})\text{As}\) system.\(^{34,35}\)

Anomalous Hall effect resulting from spontaneous magnetization is a strong proof of ferromagnetism in DMS system. Hall effect measurements were performed on selected samples. 10% of \((\text{Sr,Na})\) substitution in \((\text{Sr,Na})(\text{Cd},\text{Mn})_2\text{As}_2\) system resulted in a hole concentration of \(n_p\) equal to \(\sim 10^{20}\) cm\(^{-3}\), which was comparable to that of \((\text{Ga,Mn})\text{As}\),\(^{36}\) \((\text{In,Mn})\text{As}\),\(^{2,37}\) and \((\text{Li,Zn,Mn})\text{As}\),\(^{10}\) as shown in Fig. 4(b). The relationship between \(T_C\) and hole concentration shown by other systems suggests that increasing the charge and spin doping level would cause \((\text{Sr,Na})(\text{Cd,Mn})_2\text{As}_2\) to become magnetically ordered at a higher \(T_C\).\(^{5,26,38}\) We are currently working on optimizing the materials with the intent of demonstrating this behavior. The linear dependence of Hall resistivity with magnetic field was observed above \(T_C\). Fig. 4(c) shows the Hall resistivity of \((\text{Sr}_{0.9}\text{Na}_{0.1})(\text{Cd}_{0.9}\text{Mn}_{0.1})\text{As}_2\) at \(T = 2\) K. The anomalous Hall effect was observed at low fields (see the red arrow).

**IV. CONCLUSION**

In summary, we presented the successful synthesis and characterization of a new spin and charge-decoupled ferromagnetic DMS \((\text{Sr,Na})(\text{Cd,Mn})_2\text{As}_2\) with a layered and hexagonal CaAl\textsubscript{2}Si\textsubscript{2}-type structure. Together with carrier doping via \((\text{Sr,Na})\) substitution and spin doping via \((\text{Cd,Mn})\) substitution resulted in ferromagnetic order with \(T_C\) of up to 13 K, where the densities of charge carrier and local moments were controlled independently. The negative magnetoresistance that appeared below \(T_C\) does not scale with magnetization but shows a characteristic \(B^{1/2}\) dependence as in the case of \((\text{Ga,Mn})\text{As}\) with weak localization effect. This new DMS...
is suitable as a soft material for spin manipulation with a relatively small coercive field (less than 24 Oe) in the future. With increasing Mn doping, the interaction of the local spins and conduction electrons gave rise to a semi-metallic to insulated-like behavior. In particular, the hexagonal structure may exhibit different ferromagnetism behaviors with other previous bulk forms of DMSs, as noticed in Ref. 14, thereby providing interesting materials for future research. Moreover, the structure enables the combination of the material with topological insulators to form devices with novel functionalities.

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