Mn-induced ferromagnetism and enhanced thermoelectric properties in Ru$_{1-x}$Mn$_x$Sb$_{2+\delta}$

Hong Chang, Xin Gui, Silu Huang, Roshan Nepal, Ramakanta Chapai, Lingyi Xing, Weiwei Xie and Rongying Jin

Abstract

We report the experimental investigation of Mn doping effect on the electrical, magnetic, and thermal properties of Ru$_{1-x}$Mn$_x$Sb$_{2+\delta}$ single crystals. While RuSb$_{2+\delta}$ is a diamagnetic semiconductor, partial replacement of Ru by Mn results in ferromagnetism with the Curie temperature 536 K and 540 K for $x = 0.04$ and $0.08$, respectively. Correspondingly, the electrical resistivity decreases dramatically and shows metallic character due to the increased electron concentration. Surprisingly, the magnitude of the thermopower increases upon Mn doping, reaching $-250 \mu V K^{-1}$ at 300 K for $x = 0.08$, while the thermal conductivity remains unchanged above 100 K. These indicate a strong modification of electronic structure by doped Mn, leading to enhanced thermoelectric properties. The carriers induced by Mn not only decrease the resistivity, but also mediate the long-range ferromagnetic ordering in Ru$_{1-x}$Mn$_x$Sb$_{2+\delta}$.

Introduction

Transition-metal pnictides have attracted extensive attention in the material physics and chemistry communities for many decades because of their extremely rich physical properties, such as high-temperature superconductivity in arsenides [1], room-temperature magnetism in phosphides [2], and high-performance thermoelectricity in antimonides [3]. More recently, electronic band calculations suggest that the transition-metal (T) dipnictides (TNP$_2$) TPn$_2$, exhibit non-trivial surface states that are topologically protected [4, 5]. Given the intimate relationship between the good thermoelectricity and the topological behavior [6], this material system offers an ideal platform for exploring exotic physical properties that have potential applications.

Thermoelectric materials can convert widely distributed waste heat into electric energy or reject heat by using electrons as energy carriers [7, 8]. For TPn$_2$-type compounds, one of the unusual properties is the extremely large thermopower and the thermal conductivity at low temperatures observed in FeSb$_2$ [9–13]. This has been attributed to the strong electron–electron correlation [9, 14, 15] and the phonon–drag effect [13]. The correlation strength is expected to increase with an increasing hybridization gap [6, 15]. Although the sister material RuSb$_2$ has a larger hybridization gap [14], its thermopower at low temperatures is an order smaller than that of FeSb$_2$ [10, 12]. In addition, the magnetic response in FeSb$_2$ and RuSb$_2$ is different: the former is paramagnetic, but the latter is diamagnetic. These indicate that the physical properties in this material family are yet to be understood. Especially, none of the existing studies focus solely on RuSb$_2$, which appears always as a comparison material to FeSb$_2$. Due to stronger hybridization between Ru $d_{xy}$ orbital and Sb $p$ orbital, energy gap between $d_{xy}$ and $d_{yz/yz}$ is enlarged compared to that of FeSb$_2$ [14]. To help understand its electronic structure with the hope of improving its thermoelectric performance, we introduce Mn doping to RuSb$_2$, aiming at tuning electron correlation of Ru$_{1-x}$Mn$_x$Sb$_2$. As Mn has one less electron than Fe, the Mn-induced physical property change can be compared with that of FeSb$_2$. It turns out that the partial doping of Ru by Mn results in
the physical properties being different from that observed in FeSb₂. Based on the measurements of the electrical resistivity, Hall effect, magnetization, thermal conductivity, and thermopower of Ru₁₋ₓMnₓSb₂₊₆ (x = 0, 0.04 and 0.08), we argue that Mn doping modifies the electronic structure of the doped system, resulting in a ferromagnetic (FM) conductor with good thermoelectric properties.

**Single crystal growth and characterization methods**

Single crystalline Ru₁₋ₓMnₓSb₂₊₆ was grown using the self-flux method in a ratio of Ru:Mn:Sb = 1:x:10 (x = 0, 0.5, 1). High purity Ru, Sb, and Mn powder (Alfa Aesar) was mixed and placed in an evacuated quartz tube. The mixture was heated up to 1150 °C at the rate of 150 °C h⁻¹ and kept at 1150 °C for 36 h. After that, samples were cooled down to 700 °C at the rate of 2 °C h⁻¹ and centrifuged to remove Sb flux. The typical crystal size is about 8 × 4 × 4 mm³, as shown in the inset of figure 1(a). Single crystal x-ray diffraction (XRD) was carried out using Bruker Apex II x-ray diffractometer with Mo radiation Kα1 (λ = 0.710 73 Å). Data was collected over a full sphere of reciprocal space with 0.5° scans in ω with an exposure time of 10 s per frame. The 2θ range extended from 4° to 75°. The SMART software was used for data acquisition. Intensities were extracted and corrected for Lorentz and polarization effects with the SAINT program. Numerical absorption corrections were accomplished with XPREP, which is based on face-indexed absorption. With the SHELXTL package, the crystal structures are solved using direct methods and refined by full-matrix least squares on F². Crystal compositions were determined using the energy dispersion x-ray spectroscopy (EDX) on a Hitachi S-4500II field emission SEM. The magnetic properties were measured using a magnetic property measurement system (Quantum Design) between 1.8 and 400 K and a vibrating sample magnetometer above 300 K. The electrical resistivity, Hall effect, thermopower, and thermal conductivity were measured using a physical property measurement system (Quantum Design). The Hall signal was obtained by measuring the transverse resistivity under magnetic field reversal, i.e. \( \rho_{xy}(H) = \frac{\rho_{xy}(+H) - \rho_{xy}(-H)}{2} \).

**Results and discussion**

According to the single crystal XRD refinement, the as-grown crystals form the orthorhombic structure with the space group Pnmm (No. 58). For Mn-free single crystals, the chemical formula is RuSb₂.06, with the lattice parameters \( a = 5.952(2) \) Å, \( b = 6.679(1) \) Å, and \( c = 3.181(1) \) Å. As shown in figure 1(a), each Ru coordinates with Sb atoms, forming an octahedral environment. Excess Sb is in superposition with regular ones, as labeled by splitting Sb in figure 1(a). In figure 1(b), the single crystal XRD precession image of the \((h k 0)\) plane clearly shows such splitting as circled. The volume of the RuSb₂.06 is ~0.2% larger than the reference report [16], further indicating the existence of excess Sb. RuSb₂.06 with Sb–Sb dimers can be interpreted as the Zintl phase, in which Sb–Sb dimers form the polyanions using electrons donated from Ru to satisfy the valence requirements [17]. In the splitting Sb site, the Sb–Sb distance is even shorter, strengthening the Sb–Sb interaction. Thus, fewer
electrons are required from Ru to satisfy the valence requirement. Such atomic splitting has been observed in other systems, for example, Ca$_3$Au$_{19-x}$Ge$_x$[18].

EDX measurements also indicate that there is excess Sb in our crystals, as shown in table 1. For $x = 0$, Ru: Sb = 29.9:70.1 = 1:2.3, with Sb concentration much higher than the refined result. To check if higher Sb concentration is due to the inclusion of Sb flux in the single crystal, the large single crystal was further tested by XRD after the EDX measurements. Figure 1(c) depicts the XRD pattern, with all peaks indexed by the Pnnm structure. There is no indication of Sb inclusion. The EDX measurements were performed on two spots for each crystal, showing no discrepancy between two sets of data. Therefore, we attribute the difference between the single crystal ($\sim 20 \mu m \times 20 \mu m \times 20 \mu m$) XRD refinement and EDX measurements to systemic error between two techniques.

In the case of Mn doping, both single crystal XRD and EDX indicate that Mn partially occupies the Ru site, forming Ru$_{1-x}$Mn$_x$Sb$_{2+\delta}$. As listed in table 1, EDX measurements suggest that the actual $x = 0.04$ and 0.08 are much lower than the nominal doping values. For $x = 0.04$, the single crystal XRD refinement gives $a = 5.929$ (10) Å, $b = 6.644(11)$ Å, and $c = 3.166(5)$ Å. This corresponds to 1.2% volume reduction, reflecting much higher impact of Mn than excess Sb. Attempts to dope more Mn ($x > 0.08$) fails under the ambient condition. According to [19], the formation of MnSb$_2$ requires high pressure.

Figures 2(a) and (b) show the temperature dependence of the electrical resistivity for $x = 0, 0.04$, and 0.08 along the ab- ($\rho_{ab}$) and ac- ($\rho_{ac}$) plane, respectively. Similar to previous observation [9–11], there is a hump centered at $\sim 300$ K, and a dip around 80 K. Such non-monotonic temperature dependence of the resistivity is likely due to the combined effect in semiconductors, including thermally-activated and impurity-induced conduction [9]. With decreasing temperature, the resistivity due to thermal activation increases, while the resistivity due to impurity-induced carriers decreases. Indeed, the upturn $\rho_{ab}$ and $\rho_{ac}$ below 80 K can be described by the thermally-activated formula $\rho = \rho_0 \exp\left(\frac{E_g}{2kT}\right)$ ($\rho_0$ is a constant). We obtain the activation energy $E_g = 2.7$ meV and 5.2 meV from fitting $\rho_{ab}$ and $\rho_{ac}$, respectively. These values are about two orders

![Figure 2](image_url)
smaller than the theoretical calculations [14] and another experimental estimate [8, 9, 18]. We believe that this is due to the excess Sb, which provides in-gap density of states as discussed in Sb-deficient scenario [14].

Upon Mn doping, several features in the resistivity are worth noting. First, the resistivity becomes much smaller than the undoped case and decreases with increasing $x$. Second, the resistivity hump disappears, leading to a metallic behavior ($\frac{d\rho}{dT} > 0$) in a wide temperature range. While it is absent for $x = 0.04$, the low-temperature dip remains in the $x = 0.08$ compound, which is likely caused by inhomogeneous Mn distribution. For each $x$, $\rho_{ab}$ and $\rho_{ac}$ exhibit similar temperature profile, suggesting similar scattering mechanism in all directions. Figure 2(c) shows the temperature dependence of the resistivity anisotropy $\rho_{ab}/\rho_{ac}$. For $x = 0$, $\rho_{ab} > \rho_{ac}$ leading to $\rho_{ab}/\rho_{ac} \sim 2$ at 2 K and 4.6 at 300 K. This is not surprising because the close distance of the atoms along the $c$ direction (as reflected by the shortest lattice parameter) is in favor of the electrical conduction. Upon Mn doping, $\rho_{ab}/\rho_{ac}$ quickly reduces to ~1 for $x = 0.04$ and ~0.8 for $x = 0.08$ at room temperature. This further indicates that the doping modifies the electronic structure of Ru$_{1-x}$Mn$_x$Sb$_{2+\delta}$.

To help understand the electronic properties of Ru$_{1-x}$Mn$_x$Sb$_{2+\delta}$, we measured the Hall effect of $x = 0, 0.04,$ and 0.08. Figure 2(d) shows the field dependence of the Hall resistivity ($\rho_{xy}$) for $x = 0.08$ at $T = 20, 100, 200$ and 300 K. Note that, at a fixed temperature, $\rho_{xy}$ depends linearly on applied field with a negative slope. Similar behavior is observed in $x = 0.04$ (not shown), while $\rho_{xy}$ for $x = 0$ is slightly bent, as shown in the inset of figure 2(d) (bottom). This indicates that the doped system is electron dominated. In the inset of figure 2(d) (top), we show the temperature dependence of the carrier concentration $n = H/(e\rho_{xy})$ for $x = 0, 0.04,$ and 0.08. Note that, for $x = 0$, $n$ is in the order of $10^{15}$ cm$^{-3}$, slightly lower than in a previous report [10]. Given that the excess Sb in our material should act as an acceptor, reduced electron concentration is expected. Upon Mn doping, $n$ apparently increases with the increasing $x$. This is surprising, as Mn is expected to contribute either the same (so-called isovalent doping) or less amount of electrons than Ru$^{4+}$. As shown in table 1, our EDX measurements indicate that the Sb content is similar for $x = 0, 0.04,$ and 0.08. In this circumstance, the increase of electron concentration is likely the consequence of the modified band structure due to Mn doping.

The modification of the band structure by Mn doping is also reflected in the magnetic properties. Figure 3(a) displays the temperature dependence of the $ab$-plane magnetization $M_{ab}$ obtained by applying magnetic field $H = 1$ Tesla along the $ab$ plane for $x = 0, 0.04,$ and 0.08. Note that $M_{ab}$ of $x = 0$ is negative with little temperature dependence, indicating the diamagnetic nature of the undoped (Mn-free) system. The diamagnetism is consistent with its semiconducting electronic property, resulting mainly from the filled shells of ions. Upon Mn doping, $M_{ab}$ becomes positive below ~600 K and sharply increases below $T_C \sim 536$ K for $x = 0.04$ and ~540 K for $x = 0.08$, determined from the dip of $dM_{ab}/dT$ shown in the inset of figure 3(a). A similar behavior is observed along the $ac$ plane, as shown in figure 3(b). Similar to the electrical resistivity, there is little anisotropy in the magnetization along different directions for the doped compounds ($x = 0.04$ and 0.08), as demonstrated in figure 3(c). Furthermore, we have measured the field dependence of the magnetization at fixed temperatures. Figure 3(d) shows $M_{ab}$ versus $H$ at $T = 4$ K for $x = 0.08$. A hysteresis loop is clearly observed.

![Figure 3](image_url)
at low fields with the coercive field as ∼50 Oe. As shown in the inset of figure 3(d), $M_{sd}(H)$ exhibits linear $H$ dependence with negative slope for $x = 0$, becoming non-linear for $x = 0.04$ and 0.08, with the tendency of saturation at high fields. This indicates that Mn doping results in FM ordering below $T_C$. The magnetic moment is $∼0.008 \mu_B$/f.u. for $x = 0.04$ and $∼0.023 \mu_B$/f.u. for $x = 0.08$ at 4 K and 7 T. We estimate the effective magnetic moment per Mn as $∼0.2 \mu_B$/Mn for $x = 0.04$ and $∼0.29 \mu_B$/Mn for $x = 0.08$. Such small magnetic moment indicates dilute ferromagnetism induced by Mn doping.

In view of the above electrical and magnetic properties, it is apparent that the excess Sb reduces electrons, but Mn doping induces additional electrons into Ru$_{1-x}$Mn$_x$Sb$_{2.3}$. The latter mediates the long-rang FM interaction. There is empirical rule between the magnetization and electrical resistivity with $M = M_0 + A/\rho$ (where $M_0$ and $A$ are constants). In our case, $M_{ac}$ versus $\rho_{ac}^{-1}$ is plotted in the inset of figure 3(b), which shows indeed linear relationship for $x = 0.04$ and 0.08.

As mentioned above, the negative and giant thermopower ($S$) was observed in RuSb$_2$, with the maximum value around 10–20 K [9–13]. Figure 4(a) shows the temperature dependence of $S$ for $x = 0$ and 0.08. For $x = 0$, $S$ is positive at high temperatures but turns negative at low temperatures, with a negative maximum around 10 K, as enlarged in the inset of figure 4(a). The sign change of $S$ in our case clearly indicates that there exists both electron- and hole-type charge carriers. The positive thermopower from holes is dominant at high temperatures. The small $S$ for $x = 0$ is the consequence of the compensation from both electrons and holes. Upon Mn doping, $S$ is completely negative and reaches $−250 \mu V K^{-1}$ at 300 K. Note that the low-temperature extreme (dip) no longer exists, which further suggests the modification of electronic structure in the doped system. Similarly, as shown in figure 4(b), the low-temperature thermal conductivity peak is considerably suppressed compared to the undoped case. This is due to the enhanced scattering by the doped Mn. Interestingly, the thermal conductivity $\kappa$ is almost the same for $x = 0$ and 0.08 above 100 K, indicating the phonon dominated thermal conduction.

With the enhanced thermopower and the reduced electrical resistivity by doped Mn, we further calculate the figure of merit $ZT = TS^2/(\rho \kappa)$ for $x = 0.08$. As shown in figure 4(c), $ZT$ increases with increasing temperature, reaching 0.05 at 300 K. The improved $ZT$ is due to reduced electrical resistivity and enhanced thermopower at high temperatures in doped samples. While FM ordering in normal circumstances helps reduce scattering, thus decreasing the electrical resistivity, the weak ferromagnetism in our Ru$_{1-x}$Mn$_x$Sb$_{2.3}$ may have limited impact in thermal transport properties. The almost identical thermal conductivity above 100 K for $x = 0$ (non-magnetic) and 0.08 (magnetic) further supports the claim.

Conclusion

We have investigated the magnetic, electrical, and thermal transport properties of Ru$_{1-x}$Mn$_x$Sb$_{2.3}$ single crystals with $x = 0, 0.04$, and 0.08. For Mn-free RuSb$_2$, the splitting Sb enhances the hole concentration, resulting in small and positive thermopower at high temperatures due to the compensation with the electron contribution. However, the enhanced hole concentration enables the reduction of the electrical resistivity involving a small energy gap, indicating multiband electrical conduction. On the other hand, Mn doping effectively increases the electron concentration, driving the doped system to be metallic and FM with high Curie temperature ($∼ 536–540$ K). However, there is no evidence for the anomalous Hall effect below $T_C$, due to extremely weak ferromagnetism. The thermopower reaches $−250 \mu V K^{-1}$ for $x = 0.08$ at 300 K, corresponding to $ZT ∼ 0.05$. With this trend (increasing the value of $S$, reducing $\rho$, but constant $\kappa$ with increasing $x$), $ZT$ may be further improved if more Mn can be adapted into the system.
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ORCID iDs

Hong Chang @ https://orcid.org/0000-0001-5527-631X
Roshan Nepal @ https://orcid.org/0000-0002-1869-5395
Rongying Jin @ https://orcid.org/0000-0001-5846-4324

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