Insulator-to-metal transition and large thermoelectric effect in La$_{1-x}$Sr$_x$MnAsO

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Abstract – We report the effect of Sr substitution in an antiferromagnetic insulator LaMnAsO by the measurements of electrical resistivity, Hall coefficient, Seebeck coefficient and magnetization. Upon Sr doping to its limit $x \sim 0.10$, the room temperature resistivity drops by five orders of magnitude down to $\sim 0.01 \, \Omega \cdot \text{cm}$, and the temperature-dependent resistivity shows essentially metallic behavior. Hall and Seebeck measurements confirm consistently that the insulator-to-metal transition is due to hole doping. The room temperature Seebeck coefficient for the metallic samples is as high as $\sim 240 \, \mu \text{V}/\text{K}$, making the system a possible candidate for thermoelectric applications.

Introduction. – The quaternary compounds with ZrCuSiAs-type (abbreviated as 1111-type) structure have recently attracted much attention, primarily because of the discovery of high-temperature superconductivity in the iron arsenides [1–3]. The constituent elements in the 1111 phase belong to different groups that are called hard acid, soft acid, soft base and hard base, respectively, according to the concept of “Hard and Soft Acids and Bases” [4]. Therefore, the 1111 family holds many members owing to the combination of the four groups of elements. Up to 2008, there had been over 150 individuals synthesized [5]. Importantly, the element-selective feature in the four crystalline sites allows various kinds of successful chemical doping for inducing superconductivity in the prototype parent compound LaFeAsO [1,6–9].

The 1111 arsenides containing 3$d$ transition elements show diverse physical properties. LaMnAsO (LMAO) is an antiferromagnetic (AFM) semiconductor/insulator with a pretty high Néel temperature of 317 K [10,11]; LaFeAsO is an AFM [12] semi-metal [13], serving as a mother compound for Fe-based superconductors; LaCoAsO is an itinerant ferromagnet with a Curie temperature of 66 K [14]; and LaNiAsO is a BCS-type superconductor with transition temperature $T_c \sim 3$ K [15,16]. Fang and co-workers [17] performed first-principles calculations for the series of 1111 compounds. They were able to predict that the ground state of LMAO is an insulating antiferromagnet with the Mn moment of 3.1 $\mu_B$, consistent with the later experimental result [11].

One notes that the properties of LMAO resemble those of the parent compound of cuprate superconductors. So, it is of great interest to study its doping response. In fact, LnMnPnO ($Ln$ stands for a lanthanide, $Pn$ refers to a pnictogen including P, As and Sb) was synthesized and structurally characterized over a decade ago [18]. However, it was only after the discovery of Fe-based superconductors that there have been growing research activities on this type of material [10,11,19–26]. The apparent valence of Mn in LnMnPnO is 2+, thus the Mn ions have the electronic configuration of $d^5$, i.e., the valence electrons fill half the 3$d$ shell. Therefore, the Mn-based 1111 pnictides would be a Mott insulator, similar to the parent compound of cuprate superconductors, in the case of significant Hund’s rule coupling as well as intrasite Coulomb correlation [27]. Experiments basically agree with the point. Hosono and co-workers [19] showed that the LaMnPnO ($Pn = P$, As and Sb) thin films were all semiconducting with indirect bandgaps from 1.0 to 1.4 eV. They also demonstrated that LaMnPO was an AFM insulator with a Néel temperature up to 375 K [20].

The nominally undoped LaMnPO was an $n$-type semiconductor, and it could also be hole-doped with using

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Cu and Ca dopants, but no metallic conduction was achieved. Emery et al. [10] reported that LMAO was a $C$-type AFM semiconductor with weak ferromagnetism as well as giant magnetoresistance. For $LnMnAsO$ containing magnetic rare-earth elements, there were several investigations on the magnetic orderings (and their interactions) of Mn spins and rare-earth moments [11,23,24]; however, few doping studies have been performed. Very recently Tokura and co-workers [25] reported metallization in oxygen-deficient SmMnAsO$_{1-x}$ via electron doping. In this paper, we demonstrate an insulator-to-metal transition by hole doping in La$_{1-x}$Sr$_x$MnAsO. Surprisingly, the metallic sample has an unusually large Seebeck coefficient of $\sim 240 \mu V/K$ at room temperature (RT). This property would be attractive for thermoelectric applications.

**Experimental.** – Polycrystalline samples of La$_{1-x}$Sr$_x$MnAsO were synthesized by solid-state reaction in vacuum using powders of LaAs, SrAs and MnO. LaAs and SrAs were presynthesized, respectively, by the reaction between La/Sr and As pieces at 1023–1123 K for 20 h. The purity of all the starting materials is no less than 99.9%. Powders of LaAs, SrAs and MnO were weighed according to the stoichiometric ratios of La$_{1-x}$Sr$_x$MnAsO ($x = 0, 0.02, 0.04, 0.06, 0.08, 0.1$ and $0.12$), and thoroughly mixed in an agate mortar and pressed into pellets under a pressure of 4000 kg/cm$^2$. The pellets were loaded in a quartz-glass ampoule, and then sealed in a quartz-glass ampoule. We employed a glove box filled with protective argon atmosphere (the content of water and oxygen was below 0.1 ppm) to minimize the incorporation of excess oxygen. The ampoule was heated slowly to 1400 K in a muffle furnace, holding for 40 h and then cooled down to RT by switching off the furnace.

Powder X-ray diffraction (XRD) was carried out at RT on a D/Max-rA diffractometer with Cu-K$_\alpha$ radiation and a graphite monochromator. The XRD data were collected in a step-scan mode with an interval of 0.02$^\circ$, holding 2 seconds for each step. The scanning range was 10$^\circ$ $\leq$ 2$\theta$ $\leq$ 120$^\circ$. Lattice parameters were calculated by Rietveld refinements.

In the electrical transport measurement, the as-prepared pellets were cut and polished into thin ($\sim$0.3 mm thick) rectangular bar. Gold wires and silver paste were used for making the electrodes with the configurations suitable for the standard four-terminal resistivity ($\rho$) and Hall coefficient ($R_H$) measurements. The size of the contact pads leads to a total uncertainty in the absolute values of $\rho$ and $R_H$ of 10%. The Seebeck coefficient ($S$) was measured by a conventional steady-state technique with a temperature gradient of $\sim$0.1 K/mm, on a Quantum Design physical property measurement system (PPMS-9). The magnetization measurements were performed on a Quantum Design magnetic property measurement system (MPMS-5).

**Results and discussion.** – Figure 1(a) shows the XRD patterns of the as-prepared La$_{1-x}$Sr$_x$MnAsO samples. Most of the peaks can be well indexed by a tetragonal 1111-type unit cell with the space group $P4/nmm$. However, on close examining, several small peaks (with the intensity less than 5% of that of the strongest peak) can be detected. Figure 1(b) shows a small peak at 2$\theta$ = 42.7$^\circ$ close to the (200) reflections, which is ascribed to MnAs impurity. For the sample of $x=0.12$ (not shown here), unknown impurity phases grow substantially, suggesting that the doping limit is around $x=0.1$. The lattice constants of the undoped LMAO are refined as $a = 4.1202(5)$ Å and $c = 9.0467(10)$ Å, basically consistent with those previously reported [10,18]. With the Sr doping, the $c$-axis increases almost linearly up to $x=0.1$ in conformity with the larger size of Sr$^{2+}$ ions (compared with that of La$^{3+}$ ions), suggesting that Sr was incorporated into the LMAO lattice. It is also noted that the $c$-axis hardly changes within the measurement errors (see fig. 1(c)). The non-uniform variations in $a$ and $c$ probably reflect hole doping. On the one hand, the Coulomb electrostatic attraction between the $[\text{La}_{1-x}\text{Sr}_x\text{O}_2]^2(2-x)^+$ and $[\text{Mn}_2\text{As}_2](2-x)^-$ layers is expected to be weakened with the Sr doping, which leads to the increase in $c$-axis. On the other hand, the hole doping at the Mn sites generally tends to shrink the basal planes, canceling out the increase in $a$ by the incorporation of larger-size Sr ions.

Figure 2 shows the $\rho(T)$ data for the La$_{1-x}$Sr$_x$MnAsO polycrystalline samples. The undoped LMAO shows insulating behavior. The resistivity at RT is about 3000 $\Omega \cdot$ cm,
Fig. 2: (Colour on-line) Temperature dependence of resistivity in La$_{1-x}$Sr$_x$MnAsO, for all the samples in logarithmic scale (a), for $x=0$ and 0.1 in linear scale ((b) and (c)), for $x=0$ with the $\rho(T)$ fittings in terms of thermal activation and variable-range-hopping mechanisms ((d) and (e)), respectively. The inset of panel (a) shows the room temperature resistivity as a function of Sr doping.

Fig. 3: (Colour on-line) (a) Hall coefficient (left axis, solid symbols) and Hall carrier concentration (right axis, open symbols) of La$_{1-x}$Sr$_x$MnAsO samples with $x=0.02$ and 0.1. (b) Seebeck coefficient (left axis) and power factor (right axis) for the $x=0.1$ sample.

It is noted that a similar hole doping by Ca and Cu in LaMnPO failed to produce metallic conduction, although the RT resistivity was decreased by over three orders of magnitude [20]. The possible reason is that the solid-solution limit for Ca doping is smaller than that of Sr doping. This recalls the fact that the hole-type superconductivity could be induced in LaFeAsO only by Sr doping [5]. For the electron doping side, in comparison, an insulator-metal transition was not realized until $\delta=0.2$ in SmMnAsO$_{1-\delta}$ [25]. Therefore, the metallization in Mn-based 1111 material seems to be asymmetric to electron and hole doping. Hole doping generates a metallic state more easily.

In order to confirm and clarify the insulator-metal transition, we measured the samples’ Hall coefficient. Figure 3 shows the $R_H$ data for two representative samples: a semiconducting sample with $x=0.02$ and a metallic sample with $x=0.1$. Both samples show positive $R_H$ values in the whole temperature range, indicating that hole-type charge carriers dominate in the system. Assuming a single-band scenario, the charge carrier concentration can be estimated by $n_H = 1/(eR_H)$. So, the hole concentration for $x=0.02$ is $8.0 \times 10^{24}$ cm$^{-3}$ at RT, and it decreases rapidly with decreasing temperature. On the other hand, the estimated hole concentration at 10 K for $x=0.1$ is $1.5 \times 10^{27}$ cm$^{-3}$, and it changes hardly with temperature. The hole concentration corresponds to 0.11 holes/Mn, which meets the doping level of $x=0.10$ rather precisely. This result clearly indicates that the holes are doped via the Sr substitution in LMAO.
The Seebeck coefficients \((S)\) of \(La_{1−x}Sr_xMnAsO\) \((x = 0.02\) to 0.1) are all positive, further confirming that the charge carriers are hole-type. Figure 3(b) shows the \(S(T)\) data for the sample of \(x = 0.1\). The thermopower tends to saturate near RT, achieving 240 \(\mu V/K\), which is unusually large for a metal. It is significantly higher than that of a promising thermoelectric material Na\(_2\)CoO\(_2\) [28]. The reason for the high \(S\) value is not clear; however, it could be associated with some special Fermi surface topology in LMAO. A recent theoretical calculation for a related compound BaMn\(_2\)As\(_2\) (see the discussion below) indeed shows that the Seebeck coefficient can be over 200 \(\mu V/K\) in the case of a small hole doping [29]. The power factor, \(S^2/\rho\), is over 5 \(\mu W/(K^2 cm)\) at RT. If the material is fabricated into the form of single crystals or thin films, whose resistivity can be decreased significantly, the power factor may be increased remarkably. Thus, the system may be a potential candidate for thermoelectric applications.

We performed magnetization measurements for the \(La_{1−x}Sr_xMnAsO\) samples. A weak ferromagnetic transition at \(\sim 320\) K was seen in all the samples. This observation resembles the previous report of LMAO [10] with a small saturated moment of 0.13 \(\mu_B/\text{Mn}\). In comparison, our LMAO sample, which is “free” of MnAs impurity from XRD (see fig. 1(b)), has even smaller saturated moment of 0.04 \(\mu_B/\text{Mn}\). This suggests an extrinsic origin for the weak ferromagnetism. We further note that the sample with higher saturated magnetization contains more MnAs impurity. Since MnAs is a ferromagnet with Curie temperature at 318 K [30], we conclude that the ferromagnetic signal comes from the MnAs which has a saturated moment of 3.4 \(\mu_B/\text{Mn}\) [31]. The concentration of MnAs impurity in our samples can thus be estimated to be from 1 at.\% to 6 at.\%. This explains why the MnAs impurity sometimes cannot be found by the XRD experiments.

Generally it is possible to remove the ferromagnetic impurity contribution by measuring several isothermal \(M-H\) curves. The high-field (higher than the saturation field of the ferromagnetic impurity) \(M(H)\) slope represents the intrinsic magnetic susceptibility. For example, Johnston and co-workers [32] succeeded in extracting the intrinsic magnetization on studying BaMn\(_2\)As\(_2\) crystals containing 0.11 at.\% MnAs impurity. Figure 4 displays the extracted paramagnetic susceptibility \(\chi_p\) for \(La_{1−x}Sr_xMnAsO\). The expected intrinsic AFM transition at \(\sim 325\) K can be seen for the undoped sample, consistent with the neutron diffraction study [10,11]. The Néel temperature decreases very mildly with the Sr doping \((T_N \sim 275\) K for \(x = 0.1\)). Future experiments of neutron diffractions would be desirable to examine the Mn local moment is suppressed or not. The \(\chi_p\) values increase with increasing Sr content. This enhanced paramagnetism could be related with the magnetism of induced holes.

Here we would like to compare LMAO with its close relatives BaMn\(_2\)As\(_2\) and LaMnPO. BaMn\(_2\)As\(_2\), was identified as a G-type AFM semiconductor with a Néel temperature as high as 625 K and an ordered moment of 3.88 \(\mu_B/\text{Mn}\) [32,33]. The lowered moment (compared with a separate Mn\(^{2+}\) ion) is ascribed to the substantial Mn3d-As4p hybridizations by density functional calculations [29]. Very recently, metallization in the BaMn\(_2\)As\(_2\) system was realized by hole doping with only 5% K substitution [34,35]. The interesting result is that the local moment of Mn as well as the Néel temperature is basically preserved in the metallic doped samples. Under moderate pressures of \(\sim 5\) GPa, BaMn\(_2\)As\(_2\) also turns into a metallic state [36]. Another recent report shows evidence of metallization in LaMnPO by F doping, while the F doping hardly changes the Néel temperature and the Mn local moment [22]. In the case of LMAO, the Sr doping only mildly suppresses the magnetic order of Mn. Taken together, one may conclude that in most Mn-based paticides the doping-induced carriers dominantly have the As 4p attribute, while the local moment of 3d electrons is basically preserved.

In summary, we have demonstrated an insulator-to-metal transition by hole doping in \(La_{1−x}Sr_xMnAsO\) which is isostructural to the 1111 ferroarsenide high-temperature superconductors. Electrical resistivity data indicate that the insulator-metal transition occurs at \(x = 0.08\). The Hall coefficient measurement clearly shows that the charge carrier holes are induced by the Sr doping. The metallic samples show an unusually large Seebeck coefficient, which seems to be related to the Fermi surface topology. Thus, the system is expected to be attractive for future thermoelectric applications.

We also found that the antiferromagnetism in LMAO was relatively robust against the charge carrier doping. Therefore, it was proposed that the holes are doped mainly into the As 4p orbitals. Further theoretical and experimental investigations are called for to clarify this issue.
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