Superconductivity in \( \text{SmFe}_{1-x}M_x\text{AsO} \) (\( M = \text{Co}, \text{Rh}, \text{Ir} \))

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Abstract – In this paper we report the comparative study of superconductivity by 3\(d\) (Co), 4\(d\) (Rh), 5\(d\) (Ir) element doping in \( \text{SmFeAsO} \). X-ray diffraction patterns indicate that the material has formed the \( \text{ZrCuSiAs-type} \) structure with a space group \( P4/nmm \). It is found that the antiferromagnetic spin-density-wave (SDW) order in the parent compounds is rapidly suppressed by Co, Rh, and Ir doping, and superconductivity emerges. The diamagnetism, consistent with the \( R-T \) data, conforms to the bulk superconductivity in our \( \text{SmFe}_{1-x}M_x\text{AsO} \) (\( M = \text{Co}, \text{Rh}, \text{Ir} \)) samples. Co, Rh and Ir locate in the same column in the periodic table of the elements but have different electronic band structure, so a comparative study would add more ingredients to the underlying physics of iron-based superconductors.

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Introduction. – The discovery of superconductivity at the high temperature of 26 K in \( \text{LaFeAsO}_{1-x}\text{F}_x \) [1] last year has led to a great breakthrough in the research of high-temperature superconductivity. Soon La has been replaced by other rare-earths such as Ce, Nd, Pr, Sm to yield new superconductors with transition temperature above 50 K [2–7], which is the highest among materials except for copper oxides. These compounds have a two-dimensional \( \text{ZrCuSiAs-type} \) structure (\( P4/nmm \)) in which FeAs forms a spatial network similar to the CuO plane in the cuprate case. Nevertheless, although the crystal structure is substantially different from that of cuprate superconductors, both compounds share intriguing similarities (layered structure, doping-induced superconductivity, strong electronic correlations, and proximity of magnetic phases...). However, it is never stopped searching for new superconductors. Later the oxygen-free iron arsenide compounds \( \text{AeFe}_2\text{As}_2 \) (denoted as \( \text{FeAs-122} \), where \( \text{Ae} = \text{Ba}, \text{Sr}, \text{Ca}, \text{Eu} \) [8–13] and \( \text{LiFeAs} \) [14] were found to exhibit superconductivity.

Actually, the discovery of high-temperature superconductivity in iron-based pnictides has attracted a great deal of attention, not only because of their high critical temperatures, but also because these compounds contain the iron (Fe) element, which is a typical magnetic element and unfavorable for superconductivity with singlet pairing. Furthermore, band structure calculation indicates that the five 3\(d\)-orbitals of Fe atoms contribute to the multiple Fermi surfaces [15], so understanding the role of Fe atoms in these compounds not only helps to unveil the nature of interplay between magnetism and superconductivity, but also offers the opportunity to study the origin of superconductivity from transition metal \( d \)-band electrons. Chemical substitution is an effective method for altering the density of states at the Fermi level, and recently superconductivity in Co-doped \( \text{SmFeAsO} \) was firstly reported by our group [16], Co, Rh and Ir locate in the same column in the periodic table of elements, therefore, it seems intriguing to know whether it is possible to induce superconductivity in the \( \text{Sm-1111} \) family by substituting Fe ions with Rh or Ir, if so, are there any differences or similarities between different dopant cases? So a systematic and comparative study of different \( d \)-band element doping in the superconducting layer is helpful to understand the underlying physics in iron-based superconductors. In this paper, we report the observation of bulk superconductivity in \( \text{SmFe}_{1-x}M_x\text{AsO} \) (\( M = \text{Co}, \text{Rh}, \text{Ir} \)). Similar to the Co-doping case, Rh or Ir doping strongly destroys the anomaly in the \( \text{SmFeAsO} \) compounds and induces superconductivity. The values of the maximal superconducting transition temperatures are very close in samples doped with Co, Rh and Ir although they have very different mass. Our results suggest that superconductivity in iron-based compounds is closely related to the...
suppression of the AF order, rather than the electron-phonon coupling.

**Experimental details.** – Polycrystalline samples of SmFe$_{1-x}$M$_x$AsO (M = Co, Rh, Ir) were synthesized by the one-step solid-state reaction method using Sm, As, Fe, Fe$_2$O$_3$, and M (M = Co, Rh, Ir) as starting materials. The details of the fabrication process are described elsewhere [6,16]. The raw materials were accurately weighed according to the stoichiometric ratio of SmFe$_{1-x}$M$_x$AsO (M = Co, Rh, Ir), then thoroughly grounded and encased into pure Nb tubes. After packing, these tubes were subsequently rotary swaged and sealed in a Fe tube. The sealed samples were heated to 1180 °C and kept at this temperature for 45 hours. The high-purity argon gas was allowed to flow into the furnace during the heat-treatment process. It is noted that the sample preparation process except for annealing was performed in a glove box under high-purity argon.

The X-ray diffraction measurement was performed at room temperature with Cu-K$_\alpha$ radiation from 20° to 80° with a step of 0.01°. The analysis of X-ray powder diffraction data was done and the lattice constants were derived. Microstructure observations were performed using scanning electron microscope (SEM/EDX). The DC magnetization measurements were done with a superconducting quantum interference device (SQUID) magnetometer. The zero-field–cooled magnetization was measured by cooling the sample at zero field to 2 K, then a magnetic field was applied and the data were collected during the warming-up process. The field-cooled magnetization data was collected in the warming-up process after the sample was cooled down to 2 K at a finite magnetic field. The resistivity data were obtained using a four-probe technique on the Quantum Design instrument physical property measurement system (PPMS).

**Results and discussion.** – Figure 1 shows the X-ray diffraction patterns of the samples of SmFe$_{0.9}$Co$_{0.1}$AsO, SmFe$_{0.9}$Rh$_{0.1}$AsO, SmFe$_{0.875}$Ir$_{0.125}$AsO, which have the highest superconducting transition temperature in their own systems. It is seen that all the main peaks can be well indexed based on the ZrCuSiAs tetragonal structure with the space group $P4/nmm$, indicating that the samples are nearly single phase. There are still some small peaks coming from the second phase, as marked by the asterisks. Further analysis indicates that this tiny amount of impurity is most probably the FeAsO. By fitting the data to the structure calculated with the software XPert Plus, we got the lattice constants. In table 1, we show the $a$-axis and $c$-axis lattice parameters for the SmFe$_{1-x}$M$_x$AsO (M = Co, Rh, Ir) samples. It is clear that M doping (M = Co, Rh, Ir) leads to an apparent decrease in the $c$-axis lattice parameter while the $a$-axis one increases a bit. A similar behavior is observed in the SrFe$_{2-x}$M$_x$As$_2$ and LaFe$_{1-x}$Ir$_x$AsO compounds [17–20]. Compared to the parent compound SmFeAsO, the apparent variation of the lattice parameters upon M doping indicates a successful chemical substitution in SmFe$_{1-x}$M$_x$AsO compounds.

In order to check whether the dopants (Co, Rh and Ir here) are really doped into the lattice, the Energy Dispersive X-ray (EDX) microanalysis was performed. The insets of figs. 2(a)–(c) show the scanning electron microscope images of three typical samples with the nominal formula SmFe$_{0.9}$Co$_{0.1}$AsO, SmFe$_{0.9}$Rh$_{0.1}$AsO and SmFe$_{0.875}$Ir$_{0.125}$AsO. Clearly, the samples seem denser though there are several voids observed. In addition, multiple layers forming a large grain of the superconducting phase can be easily detected in the samples, indicating a layer growth mechanism. Typical EDX spectra of the above-mentioned samples are presented in the main panel of figs. 2(a)–(c). The analyzed results are also shown in table 2. The grains with layered structures selected to take the EDX spectra are marked by little rectangles. In

![Figure 1:](image-url) (Color online) XRD patterns of the SmFe$_{1-x}$M$_x$AsO (M = Co, Rh, Ir) samples. The impurity phases are marked by *.

| Table 1: $a$- and $c$-axis lattice constants of SmFe$_{0.9}$Co$_{0.1}$AsO, SmFe$_{0.9}$Rh$_{0.1}$AsO, and SmFe$_{0.875}$Ir$_{0.125}$AsO. |
|-------------------|---------|---------|
| **Nominal**       | $a$ (Å) | $c$ (Å) |
| SmFeAsO           | 3.9391  | 8.4970  |
| SmFe$_{0.9}$Co$_{0.1}$AsO | 3.9412  | 8.4802  |
| SmFe$_{0.9}$Rh$_{0.1}$AsO | 3.9427  | 8.4501  |
| SmFe$_{0.875}$Ir$_{0.125}$AsO | 3.9521  | 8.4190  |

| Table 2: Atomic ratio of the elements for the samples SmFe$_{0.9}$Co$_{0.1}$AsO, SmFe$_{0.9}$Rh$_{0.1}$AsO, and SmFe$_{0.875}$Ir$_{0.125}$AsO. |
|-------------------|-----|-----|-----|-----|-----|
| **Element**       | O   | As  | Sm  | Fe  | M   |
| SmFe$_{0.9}$Co$_{0.1}$AsO | 27.43 | 24.86 | 23.95 | 20.60 | 3.15 |
| SmFe$_{0.9}$Rh$_{0.1}$AsO | 28.71 | 28.33 | 22.68 | 18.18 | 2.10 |
| SmFe$_{0.875}$Ir$_{0.125}$AsO | 23.11 | 23.80 | 27.11 | 24.65 | 1.33 |
Fig. 2: (Color online) The energy dispersive X-ray microanalysis (EDX) spectra of the samples (a) SmFe$_{0.9}$Co$_{0.1}$AsO, (b) SmFe$_{0.9}$Rh$_{0.1}$AsO, (c) SmFe$_{0.875}$Ir$_{0.125}$AsO. The insets show the scanning electron microscopic (SEM) picture. The little rectangles mark the positions where we took the EDX spectra.

In most cases, the dopants (Co, Rh and Pd) can be easily found in the corresponding grains, and the true doping levels are close to the nominal ones. It should be noted that the same was found for other nominal compositions of the samples.

Figure 3 shows the temperature dependence of the electrical resistivity for SmFe$_{1-x}$M$_x$AsO (M = Rh, Ir) samples in the temperature range from 300 to 2 K (electrical resistivity of SmFe$_{1-x}$Co$_x$AsO not shown here). The inset shows an enlarged plot of $\rho$ vs. $T$ at low temperature. It is known that the undoped SmFeAsO sample exhibits a clear anomaly near 150 K [2], which is ascribed to the spin-density-wave (SDW) instability and structural phase transitions from tetragonal to orthorhombic symmetry. As seen from fig. 3(a), by doping with Rh, the SDW transition is suppressed and the resistivity drop was converted to an uprisng at lower temperature; superconductivity at $\sim 6.7$ K appears in the sample with nominal composition $x = 0.05$. At higher Rh doping, the uprisng at lower temperature is not obvious, and the highest transition temperature 12.3 K is observed at $x = 0.10$. This is similar to the case of Co doping in the iron oxyarsenides compounds [21, 22]. With further Rh doping, the transition temperature decreases (4.8 K for $x = 0.15$) and disappears again at $x = 0.20$. Similar to SmFe$_{1-x}$Rh$_x$AsO, the resistivity of SmFe$_{1-x}$Ir$_x$AsO samples changes from semiconductorlike to superconducting with the Ir doping (see fig. 3(b)), and the
highest transition temperature 19 K appears at \( x = 0.125 \). Our data demonstrate that similar to Co doping, both 4d (Rh) and 5d (Ir) elements doping could suppress the SDW transition and induce superconductivity in the Sm-1111 system.

We measured the ac magnetic susceptibility to further confirm the superconductivity of SmFe\(_{1-x}\)M\(_x\)AsO (M = Co, Rh, Ir). Figure 4 shows the temperature dependence of DC magnetization for SmFe\(_{0.9}\)Co\(_{0.1}\)AsO, SmFe\(_{0.9}\)Rh\(_{0.1}\)AsO, and SmFe\(_{0.875}\)Ir\(_{0.125}\)AsO samples. The measurement was carried out under a magnetic field of 10 Oe in zero-field-cooled and field-cooled processes. The samples show a well diamagnetic signal and superconductivity with \( T_c = 15.6 \) K for SmFe\(_{0.9}\)Co\(_{0.1}\)AsO, \( T_c = 9.6 \) K for SmFe\(_{0.9}\)Rh\(_{0.1}\)AsO, and \( T_c = 16.5 \) K for SmFe\(_{0.875}\)Ir\(_{0.125}\)AsO, which correspond to the middle transition point of resistance, a superconducting volume fraction is large enough to constitute bulk superconductivity. In the inset of figs. 4(a)–(c) we present the fraction is large enough to constitute bulk superconductivity. In the inset of figs. 4(a)–(c) we present the rough superconducting phase diagram in SmFe\(_{1-x}\)M\(_x\)AsO (M = Co, Rh, Ir). A dome-like \( T_c(x) \) curve can be seen, which is similar to other iron-based superconductors [1–5].

Figure 5 shows the temperature dependence of resistivity for SmFe\(_{0.9}\)Co\(_{0.1}\)AsO, SmFe\(_{0.9}\)Rh\(_{0.1}\)AsO and SmFe\(_{0.875}\)Ir\(_{0.125}\)AsO samples under different magnetic fields. Similar to other iron-based superconductors, the applied magnetic field is observed to suppress the transition. It is clear that the onset transition temperature is not sensitive to the magnetic field, but the zero-resistance point shifts more quickly to lower temperatures. We tried to estimate the upper critical field \( (H_{c2}) \), using 90% points on the resistive transition curves. The change of transition temperature \( (T_c) \) with critical field \( (H) \) is shown in fig. 5(d). The slope of \( -dH_{c2}/dT \) is 4.5 T/K for SmFe\(_{0.9}\)Co\(_{0.1}\)AsO, 3.6 T/K for SmFe\(_{0.9}\)Rh\(_{0.1}\)AsO and 4.2 T/K for SmFe\(_{0.875}\)Ir\(_{0.125}\)AsO, respectively. From this figure, using the Werthamer-Helfand-Hohenberg (WHH) formula [23], \( H_{c2}(0) = 0.693 \times (dH_{c2}/dT) \times T_c \), we can get \( H_{c2}(0) \) is about 48 T for SmFe\(_{0.9}\)Co\(_{0.1}\)AsO. Similarly, we could get \( H_{c2}(0) = 25.6 \) T for SmFe\(_{0.9}\)Rh\(_{0.1}\)AsO, and 51 T for SmFe\(_{0.875}\)Ir\(_{0.125}\)AsO, respectively. If one adopts a criterion of 99% \( \rho_0(T) \) instead of 90% \( \rho_0(T) \), the \( H_{c2}(0) \) value of this sample obtained by this equation is even higher.

The discovery of superconductivity in iron-based compounds has stimulated a massive experimental and theoretical effort to uncover the mechanisms responsible for this novel superconductivity; however, the superconductivity mechanism in these new superconductors remains unclear yet. It is interesting that superconductivity was realized by doping the magnetic element cobalt into the superconducting-active Fe\(_{1−x}\)As layers, and our results indicate that not only 3d (Co) element doping, but also 4d (Rh) and 5d (Ir) elements doping could suppress the SDW transition and induce superconductivity in the Sm-1111 system. It should be noted that Co, Rh and Ir locate in the same column in the periodic table of the elements; however, they have different electronic band structure and masses. Regarding the close maximal superconducting transition temperature in samples doped with Co, Rh and Ir, we argue that the superconductivity

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Fig. 4: Temperature dependence of DC magnetization for the sample (a) SmFe\(_{0.9}\)Co\(_{0.1}\)AsO, (b) SmFe\(_{0.9}\)Rh\(_{0.1}\)AsO, (c) SmFe\(_{0.875}\)Ir\(_{0.125}\)AsO. Inset: the superconducting phase diagram in SmFe\(_{1-x}\)M\(_x\)AsO (M = Co, Rh, Ir).

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is closely related to the suppression of the AF order, rather than the electron coupling. A similar conclusion was also drawn for the Sr-122 system. Our results suggest that a comparative study would give us important clues to understanding the superconducting mechanisms on iron-based superconductors.

Conclusions. – In summary, we have successfully fabricated a series of new superconductors SmFe$_{1-x}$M$_x$AsO ($M = \text{Co, Rh, Ir}$) by replacing Fe with 3$d$ (Co), 4$d$ (Rh), 5$d$ (Ir) elements. X-ray diffraction patterns indicate that the material has formed the ZrCuSiAs-type structure. The presence of zero resistance and diamagnetism in the measurement proves that the M ($M = \text{Co, Rh, Ir}$) substitution in the SmFeAsO compounds leads to superconductivity. Furthermore, through measuring the electrical resistivity under different magnetic fields, we found that the superconductivity in all the doped samples is rather robust against the magnetic field. Considering the location of Co, Rh, Ir in the same column in the periodic table of the elements, a comparative study is helpful to understand the underlying physics in iron-based superconductors.

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