Superconductivity induced by doping Rh in CaFe$_{2-x}$Rh$_x$As$_2$

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Abstract. In this paper, we report the synthesis of iron-based superconductors CaFe$_{2-x}$Rh$_x$As$_2$ using a one-step solid state reaction method that crystallizes in the ThCr$_2$Si$_2$-type structure with a space group I4/mmm. The systematic evolution of the lattice constants demonstrates that the Fe ions are successfully replaced by the Rh. By increasing the doping content of Rh, the spin–density–wave (SDW) transition in the parent compound is suppressed and superconductivity emerges. The maximum superconducting transition temperature is found at 18.5 K with a doping level of $x = 0.15$. The temperature dependence of dc magnetization confirms superconducting transitions at around 15 K. The general phase diagram was obtained and found to be similar to the case of the Rh-doping Sr122 system. Our results explicitly demonstrate the feasibility of inducing superconductivity in Ca122 compounds by higher d-orbital electron doping; however, different Rh-doping effects between FeAs122 compounds and FeAs1111 systems still remains an open question.
1. Introduction

The discovery of iron pnictide superconductors [1] has broken cuprate ‘monopoly’ in the physics of high-temperature superconductivity (HTSC) compounds, and it has revived the hopes both on further progress in this field related to the synthesis of new perspective high-temperature superconductors as well as on a more deep understanding of mechanisms of HTSC. Up to now, five homologous series of iron-based superconductors have been discovered, commonly denoted as 1111 phase (REFeAsO with RE = rare earth) [2]–[6], 122 phase (AEFe$_2$As$_2$ with AE = alkaline earth) [7]–[10], 111 phase (AEFeAs with A = alkali metal) [11, 12] and 11 phase (FeTe or FeSe) [13], 42622 phase (Sr$_2$Sc$_2$O$_6$Fe$_2$P$_2$, Sr$_2$V$_2$O$_6$Fe$_2$As$_2$, etc) [14, 15]. In these compounds, the Fe–As layer is thought to be responsible for superconductivity, which is separated by different carrier reservoir layers, such as RE-O, AE and A.

The parent CaFe$_2$As$_2$ has the tetragonal ThCrSi-type crystal structure with a space group I4/mmm, similar to other members of the AeFe$_2$As$_2$ family. At ambient pressure, CaFe$_2$As$_2$ undergoes a transition from a non-magnetically ordered tetragonal to an antiferromagnetic orthorhombic phase [16, 17]. Doping or applied pressure could suppress this transition and induce the superconductivity [18]–[20]. In this paper, we investigate Rh-doping effect in the Ca122 system. Rhodium is a 4d metal that is located just below Co and above Ir in the periodic table of elements. For Rh-doping, a suppression of the SDW state and emergence of superconductivity have been reported in (Ba, Sr)Fe$_2$As$_2$ and the Re1111 system [21]–[25]. Now we report the successful synthesis of the new superconductor CaFe$_{2-x}$Rh$_x$As$_2$ with a $T_c$ of 18 K. X-ray diffraction indicates that the material has formed the ThCr$_2$Si$_2$-type structure with a space group I4/mmm. Resistivity, dc magnetic susceptibility as well as the phase diagram have been determined in the system of CaFe$_{2-x}$Rh$_x$As$_2$.

2. Experimental

We employed a one-step solid state reaction method to synthesize the CaFe$_{2-x}$Rh$_x$As$_2$ samples. The details of fabrication process are described elsewhere [30]. Stoichiometric amounts of the starting elements Ca, Fe, Rh and As were thoroughly grounded and encased into pure Nb tubes. After packing, this tube was subsequently rotary swaged and sealed in a Fe tube. The sealed samples were heated to 850°C and kept at this temperature for 35 h. Then they were cooled down slowly to room temperature. The high-purity argon gas was allowed to flow into the furnace during the heat-treatment process. The sintered samples were obtained by breaking the Nb tube. It is noted that all of the weighing, mixing and encasing procedures were performed in a glove box containing a high-purity argon atmosphere.
3. Results and discussion

In order to have a comprehensive understanding of the evolution induced by the doping process, we have measured the x-ray diffraction patterns for all samples. Figure 1 shows the representative XRD patterns of CaFe$_{2-x}$Rh$_x$As$_2$ samples ($x = 0.0$ and $0.1$). The XRD peaks can be well indexed based on a tetragonal cell of ThCr$_2$Si$_2$-type structure, indicating that the samples are essentially single phase. Small amounts of impurity phases, mostly perhaps FeAs, were also observed in the XRD patterns. By fitting the data to the structure calculated with the software X’Pert Plus, we obtain the lattice constants. The lattice parameters are plotted in figure 2 as a function of Rh content. In the parent phase CaFe$_2$As$_2$, the lattice constants are $a = 0.3887$ nm and $c = 1.1731$ nm, which are in agreement with previous reports [9, 16, 17]. With increasing Rh content, the $a$-axis lattice constant expands a bit, while the $c$-axis shrinks significantly. The change in lattice parameters of in CaFe$_{2-x}$Rh$_x$As$_2$ compounds is similar to the
Figure 2. Lattice parameters as a function of Rh content. It is clear that the $a$-axis lattice expands, while the $c$-axis lattice shrinks with Rh substitution.

The nearly linear variation in the lattice parameters indicates a successful chemical substitution. The case of doping the Fe with Ru, Ir or Pd in iron-based superconductors [21, 22], [26]–[28]. The nearly linear variation in the lattice parameters indicates a successful chemical substitution.

Figure 3 shows the temperature dependence of the electrical resistivity for CaFe$_{2-x}$Rh$_x$As$_2$ samples with $x = 0$–0.3, respectively. Data are shown normalized by the room-temperature resistivity $R_{300\,\text{K}}$, to remove uncertainty in estimates of the absolute value due to geometric factors. Successive datasets are offset vertically by 1 for clarity. The parent phase exhibits a resistivity anomaly at about 165 K, which is associated with the magnetic/structural phase transition. The anomaly is clearly suppressed in temperature with increasing $x$. For the samples with $x > 0.05$, superconductivity is evident from a drop in resistivity, while the anomaly associated with structural/magnetic phase transition is still observable in the normal state. With a further increase in Rh fraction, the resistivity anomaly disappeared completely and the superconducting critical temperature $T_c$ reaches the highest value of 18.5 K in the sample with $x = 0.15$, which is comparable to the value of Rh-doping (Ba,Sr)122 system [21, 22]. Figure 5(a) shows an enlarged plot of $R$ versus $T$ for CaFe$_{1.85}$Ru$_{0.15}$As$_2$ at low temperature. It is clear that the resistivity vanishes at about 7 K. It is noted that the resistivity drop was not converted to an uprising with the Rh doping, which is different from the Co- or
Figure 3. Temperature dependence of resistivity for the CaFe$_{2-x}$Rh$_x$As$_2$ samples measured in zero field. Data are normalized to $R_{300\,\text{K}}$.

Figure 4. Temperature dependence of dc magnetization for the CaFe$_{2-x}$Rh$_x$As$_2$ samples. The measurements were performed under a magnetic field of 20 Oe with zero-field-cooled and field-cooled modes.

Pd-doped samples [21, 29]. This difference may be induced by the two effects that give opposite contributions to the resistivity in the system: the decrease in the scattering rate as well as the charge carrier densities. In addition, the normal state resistivity of the superconducting sample shows a roughly linear behavior, starting just above $T_c$ all the way up to 300 K.
Figure 5. Temperature dependence of resistivity (a) and dc magnetization (b) at low temperature for the CaFe$_{0.85}$Rh$_{0.15}$As$_2$ samples.

Figure 4 shows the temperature dependence of the dc magnetization for the CaFe$_{2-x}$Rh$_x$As$_2$ samples. The measurement was carried out under a magnetic field of 20 Oe in the zero-field-cooled and field-cooled processes. We compare the diamagnetic signals in the samples with $x = 0.05$, 0.10, 0.15, 0.20 and 0.25. A clear diamagnetic signal appears around 15 K in the samples, which correspond to the middle transition temperature of the resistivity data. Figure 5(b) shows M–T pattern for the sample $x = 0.15$. The diamagnetism and presence of zero resistance in the samples are the proof that Rh substitution in the CaFe$_2$As$_2$ compounds lead to superconductivity. Although the connectivity between grains in our polycrystalline samples as well as the vortex pinning effect give the same influence on the diamagnetization signal, the strong diamagnetization value certainly indicates a rather large volume of superconductivity.

It is well known that CaFe$_2$As$_2$ undergoes a transition from a non-magnetically ordered tetragonal to an antiferromagnetic orthorhombic phase at ambient pressure; however, neutron
powder diffraction measurements of CaFe$_2$As$_2$ under hydrostatic pressure found that for $p > 0.35$ GPa (at $T = 50$ K), the antiferromagnetic orthorhombic phase transforms to a new, non-magnetically ordered, collapsed tetragonal structure. When the sample is cooled across the tetragonal-collapsed tetragonal phase transition, there is an extremely anisotropic change in the unit cell dimensions: the $a$-axis expands by 2.5% and the $c$-axis contracts by 9% [9], [16]–[20]. However, lattice parameter variation is found in the Rh-doping Ca$_{122}$ system. In the compound $x = 0.3$, for example, the $c$-axis lattice parameter decrease is 2%. However, $a$-axis lattice parameters increase only by about 1%. We suspect that the $c$-axis shrinkage effect occurring in this Ca$_{122}$ system could add charge carriers as well as chemical pressure. However, which of these effects is more important for superconductivity requires further exploration, as does their possible interplay.

Based on the measurements described above, we can establish a composition-temperature phase diagram for CaFe$_{2-x}$Rh$_x$As$_2$, as shown in figure 6. Both $T_{an}$ and $T_c$ were defined as the temperature in which the anomaly appears in resistivity and the superconducting transition, respectively. With increasing Rh-doping, the temperature of the anomaly is driven down, and the superconducting state emerges at $x = 0.05$, and reaching a highest $T_c$ of 18.5 K at $x = 0.15$, the superconducting state continues from $x = 0.05$, and even appears at the doping level of $x = 0.3$. This general phase diagram looks very similar to that of Co doping [29]. Considering Rh is located just below Co and above Ir in the periodic table of elements, we would conclude that the superconductivity induced by Rh-doping shares the similarity as that of Co- or Ir-doping. It should be noted that there exists a region in which the SDW and superconductivity co-exist. This result is different from Rh-doping FeAs$_{1111}$ superconductors, in which no coexistence of antiferromagnetism and superconductivity in an underdoped region is found [24]. Thus, further experimental and theoretical work is needed for the interpretation of the different properties between the FeAs$_{1111}$-type superconductors and the FeAs$_{122}$-type superconductors.

Figure 6. Electronic phase diagram for CaFe$_{2-x}$Rh$_x$As$_2$. $T_{an}$ and $T_c$ denote the resistivity anomaly temperature and the critical transition temperature, respectively. The dashed line provides a guide to the eye for the possible SDW/structural transitions near the optimal doping level.
4. Conclusions

In summary, we have synthesized a series of layered CaFe$_{2-x}$Rh$_x$As$_2$ compounds with ThCr$_2$Si$_2$-type structure. The systematic evolution of the lattice constants indicates successful Rh-doping into the lattice. The diamagnetism and presence of zero resistance in the samples are the proof that Rh substitution in the CaFe$_2$As$_2$ compounds lead to superconductivity. A detailed phase diagram with evolution from SDW to superconducting state with Rh-doping is given.

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