Superconductivity at 14K in the Co-doped SmFe$_{0.9}$Co$_{0.1}$AsO

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ABSTRACT

We report superconductivity in the SmFe$_{0.9}$Co$_{0.1}$AsO system being prepared by most easy and versatile single step solid-state reaction route. The parent compound SmFeAsO is non-superconducting but shows the spin density wave (SDW) like antiferromagnetic ordering at around 140K. To destroy the antiferromagnetic ordering and to induce the superconductivity in the parent system, the Fe$^{2+}$ is substituted partially by Co$^{3+}$. Superconductivity appears in SmFe$_{0.9}$Co$_{0.1}$AsO system at around 14K. The Co doping suppresses the SDW anomaly in the parent compound and induces the superconductivity. Magnetization measurements show clearly the onset of superconductivity with $T_c^{\text{dia}}$ at 14K. The isothermal magnetization measurements exhibit the lower critical fields ($H_{c1}$) to be around 200Oe at 2 K. The bulk superconductivity of the studied SmFe$_{0.9}$Co$_{0.1}$AsO sample is further established by open diamagnetic $M(H)$ loops at 2, and 5K. Normal state (above $T_c$) linear isothermal magnetization $M(H)$ plots excluded presence of any ordered magnetic impurity in the studied compound.

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Key Words: Oxypnictides superconductivity, SmFe$_{0.9}$Co$_{0.1}$AsO system, and Magnetization

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INTRODUCTION

The recent discovery of superconductivity at 26K in LaFeAsO$_{1-x}$F$_x$ and the subsequent findings of the enhanced $T_c$ up to 56K have attracted a great deal of attraction, in particular from the superconductors scientific community [1-5]. The parent compounds of this new superconductor ReFeAsO (Re = La, Pr, Sm, Gd, Nd, Ce etc.) have a quasi two-dimensional tetragonal layered structure. The Fe-As layer is usually thought to be responsible for superconductivity and the Re-O layer is a carrier reservoir layer to provide electron/hole carriers in ReFeAsO compounds. The parent compounds of this family do not show superconductivity at all and rather exhibits an anomaly in resistivity measurement attributed to spin density wave (SDW) characteristic [6,7]. The doping of electrons/hole carriers into the Fe-As layer leads to the suppression of the long range SDW order and to the subsequent induction of the superconductivity in these compounds [1-5,8-10]. The doping of electrons is achieved either by oxygen deficiency or by fluorine (F) doping [1-5,8,10]. The former can be achieved by high pressure high temperature (HPHT) only and later by either HPHT or quartz encapsulation coupled with high temperature heat treatment. Interestingly HPHT (6 Gpa, 1400 °C) is not readily available in most laboratories and the fluorine corrodes with the quartz at high temperatures. Hence, in principle it is getting difficult for material scientists to synthesize these superconductors. Recently Sefat et al [11] and Qi et al [12] have come up with an idea to induce superconductivity in these Iron-Arsenide compounds by doping of electrons through Fe$^{2+}$ site Co$^{3+}$ substitution in the Fe-As layer. We followed this and achieved bulk superconductivity at about 14K in SmFe$_{0.9}$Co$_{0.1}$AsO sample. The SDW characteristic of the SmFeAsO was suppressed by Co doping and superconductivity was induced at around 14K.

EXPERIMENTAL

Polycrystalline SmFeAsO and SmFe$_{0.9}$Co$_{0.1}$AsO samples were synthesized by single step solid-state reaction method. Stoichiometric amounts of Sm, Fe, As, Co$_3$O$_4$
and Fe₂O₃ were thoroughly ground. It is to be noted that weighing and grinding was done in the glove box under high purity argon atmosphere. The powder was then palletized and vacuum-sealed in a quartz tube. Roughly the vacuum was of the order of 10⁻⁴ Torr. Subsequently this sealed quartz ampoule was placed in box furnace and heat treated at 550°C for 12 hours, 850°C for 12 hours and then finally 1150°C for 33 hours in continuum. Then furnace was allowed to cool naturally. The sintered sample was obtained by breaking the quartz tube. The obtained sample is black in color and bit brittle, in fact it is nearly in powder form. Room temperature X-ray diffraction pattern was obtained using CuKα radiation on Desktop Rigaku-miniflex II diffractometer. The magnetization measurements were carried out on Quantum Design magnetic property measurement system (MPMS).

RESULTS AND DISCUSSION

Figure 1 shows the room temperature XRD patterns for SmFeAsO and SmFe₀.₉Co₀.₁AsO samples along with their Rietveld refinements. It is observed that all main peaks can be well indexed based on the basis of space group P4/nmm. Further, besides the majority phase (tetragonal P4/nmm) an extra peak at around 27.80 degree having low intensity (marked with *) is also seen in the XRD pattern of SmFe₀.₉Co₀.₁AsO sample. All the permitted diffraction planes of the ReFeAsO system are marked with green vertical lines between the observed/fitted patterns and their difference in the bottom. It can be noted that except the * marked peak at 27.80 degree all other observed peaks match with the identified green marked planes of the system. The same impurity is seen for SmFe₀.₉Co₀.₁AsO in ref. 12 as well. The structure of SmFeAsO and SmFe₀.₉Co₀.₁AsO at 300 K is refined with the tetragonal space group P4/nmm. Sm and As atoms are located at Wyckoff positions 2c, O is situated at 2a and Fe/Co are shared at site 2b. The Lattice parameters for SmFe₀.₉Co₀.₁AsO are found to be a = 3.9398 (7) Å and c = 8.4639 (4) Å. While for the parent compound the lattice parameters are a = 3.9375 (6) Å and c = 8.5021 (4) Å. It is clear that the c lattice parameter decreases with Co doping, while the a-axis remains nearly unaltered. The decrease in c lattice parameter suggests
that Co has gone in the tri-valence Co\textsuperscript{3+} state at the place of Fe\textsuperscript{2+}, because ionic size of Co\textsuperscript{3+} is smaller than Fe\textsuperscript{2+}. This substitution of Co\textsuperscript{3+} at the site of Fe\textsuperscript{2+} increases electron carriers in Fe-As layer, which in turn induces the superconductivity in Co doped SmFeAsO, is to be discussed next. The electrical and thermal characterization of the pristine SmFeAsO has already been reported by some of us in ref.7. This compound clearly exhibited a SDW character below 150K. Further in SmFeAsO, the Sm\textsuperscript{3+} ions ordered anti-Ferro magnetically (AFM) and superconductivity was not observed down to 2K, for details see ref. 7.

The temperature dependence of magnetic susceptibility, measured in both zero-field-cooled (ZFC) and field-cooled (FC) conditions at 10Oe for SmFe\textsubscript{0.9}Co\textsubscript{0.1}AsO is represented in figure 2. Although the transition is broad, both ZFC and FC clearly indicate the transition of the compound to a superconducting state below 14K. The magnetic signal comes out to be negative below 14K. The onset temperature of superconducting transition $T_c^{\text{dia}}$ for SmFe\textsubscript{0.9}Co\textsubscript{0.1}AsO is hence considered at 14K. The magnitude of the magnetic signal confirms the bulk superconductivity in our sample. As far as the volume fraction of superconductivity is concerned, the signal magnitude is slightly better than as in ref. 11 for LaFe\textsubscript{0.89}Co\textsubscript{0.11}AsO and in ref. 12 for SmFe\textsubscript{0.9}Co\textsubscript{0.1}AsO. Also as rightly pointed out in ref.11, the determination of superconducting volume fraction on sintered polycrystalline samples had always been tricky due to pinning and penetration effects. Never the less we can safely conclude that the presently studied single step synthesized SmFe\textsubscript{0.9}Co\textsubscript{0.1}AsO sample is superconducting below 14K, and is in confirmation with the results shown in ref. 11 and ref. 12. Interestingly although the optimum superconducting transition temperature ($T_c$) for the doped (either by flourine or oxygen vacancy) LaFeAsO and SmFeAsO are around 30 and 55K respectively [1,5], with Co doping both are superconducting below about 14K [11,12]. In another very recent report on Co doped CeFeAsO, superconductivity is observed below 11.3K [13]. It is clear that in Co doped samples neither the optimum $T_c$ nor the obvious Re ionic size effect [1,5,14] are yet established [6,7,13]. We believe the possible reasoning behind the same could be disorder in superconducting Fe-As block due to Fe\textsuperscript{2+}/Co\textsuperscript{3+} substitution. Although the Co\textsuperscript{3+} substitution at Fe\textsuperscript{2+} site in Fe-As layer
provides the required mobile electrons but creates disorder as well in the superconductivity layer. It is also to be noted, that although bulk superconductivity in terms of diamagnetic transitions is seen in both ref. 11 and in presently studied sample, the volume fraction is seemingly less and can not be left without discussion, as suggested in ref.11. Though Co substitution at Fe site induces superconductivity in Fe-As based oxy-arsenides by electron doping, the same induces disorder and hence the superconductivity is weak and not optimized. Seemingly there is a competition between direct carrier introduced (Fe$^{2+}$/Co$^{3+}$) superconductivity and the disorder thus created. Or otherwise principally 10% substitution of O$^2$ by F$^1$ or oxygen vacancies of around 15% must yield the similar result with same amount of Co$^{3+}$ at Fe$^{2+}$ site. Another important possibility still to be probed is exact amount of doped Co$^{3+}$, some of the substituted Co may be in +2 state as well, and hence ineffective in doping electrons. In any case even by varying the Co content in LaFe$_{1-x}$Co$_x$AsO, the optimized $T_c$ is achieved only up to 14K[11]

Inset of figure 2 shows the isothermal magnetization $M(H)$ curve of SmFe$_{0.9}$Co$_{0.1}$AsO at 2, 5, 7, and 9K. The lower critical field values are seen at around 200, 150, 100 and 500e at 2, 5, 7, and 9K respectively. Again confirming the bulk nature of superconductivity in the studied SmFe$_{0.9}$Co$_{0.1}$AsO. The complete isothermal magnetization loops of the studied SmFe$_{0.9}$Co$_{0.1}$AsO at 2 and 5K are shown in figure 3. These plots also point towards the bulk superconductivity of the studied compound. The critical current density roughly estimated from the observed $M(H)$ loops in figure 3 is around $10^3$A/cm$^2$ at 2K and 200Oe applied field.

Figure 4 depicts the isothermal magnetization $M(H)$ plots of the SmFe$_{0.9}$Co$_{0.1}$AsO at 50 and 100K, i.e. well above the superconductivity transition temperature of 14K, in applied fields of up to 50KOe. This is to check the possibility of any magnetically ordered impurity phase in the compound particularly in terms of Fe or Co derivatives. As see seen from the two plots at 100 and 50K, the $M(H)$ behavior is linear up till to 5KOe, with only very small remnant moment of around 0.004 emu/g. This value is slightly higher than as observed for the HPHT synthesized SmFeAsO$_{0.85}$ ($T_c$ ~52.4K), but still close [14]. This observation rules out any magnetic impurity in our
The magnetic moment versus temperature i.e., $M(T)$ plot of the sample in its normal state is exhibited in inset of figure 4. The plot does not follow the Curie-Weiss law and rather show a linear behavior down to at least 100K, later there seems to be an up-turn. The situation is similar to that as in ref.14, with small low $T$ up turn in our sample and slightly higher moment, which may arise due to 10% Co being doped in our sample. The linearity of Sm$^{3+}$ moment can be attributed to Van Vleck ion, being seen in many other Sm compounds as well [15].

In present case the carriers are directly doped within the Fe-As layer via Co doping. Here, the substitution of Co$^{3+}$ at the place of Fe$^{2+}$ in Fe-As superconducting layer provides directly the free mobile electron in this layer and thus suppresses the magnetic $SDW$ ordering and stimulate the superconductivity. This is considered as an alternative way to introduce the charge carriers in Fe-As layer without using the fluorine doping or creation of the oxygen vacancies in the charge reservoir Re-O layer. However the transition temperature is low and the volume fraction of superconductivity is also less in comparison to fluorine doped or oxygen deficient samples prepared by $HPHT$ technique [14,16-18]. On an $HPHT$ synthesized SmFeAsO$_{0.85}$, a $T_c$ of 52.4K is reported with the diamagnetic moment signal at 5K, which is about seven times more than that of the presently studied sample [14]. The less volume fraction in the Co substitution induced superconductor can be attributed to the presence of sufficient disorder produced by Co$^{3+}$ doping at Fe$^{2+}$ site in superconducting layer. Interestingly the same does not hold ground for two-layered MFe$_2$As$_2$ compound (M = Ca, Sr, Ba or divalent Eu), which exhibits reasonably good superconductivity with Co substitution at Fe site [19]. Perhaps the role of disorder is more prominent in single layered ReFeAsO compounds. Or otherwise the Co substitution induced superconductivity in ReFeAsO [11] is yet far from optimized. As far as the volume fraction and shape of the diamagnetic plots are concerned, our results are close to that as observed in ref. 11 by A. Sefat et al.

In summary, we have successfully synthesized the iron based Co-doped layered compound SmFe$_{1-x}$Co$_x$AsO ($x = 0$ & 0.10) by an easy one step solid-state reaction route. Co doping is an effective way to introduce charge carriers in Fe-As layer to bring out the superconductivity in ReFeAsO system. The challenge between competing direct carrier
introduced (Fe$^{2+}$/Co$^{3+}$) superconductivity and the disorder thus created is yet to be resolved.

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FIGURE CAPTIONS

Fig 1: Fitted and observed room temperature X-ray diffraction patterns of SmFeAsO and SmFe$_{0.9}$Co$_{0.1}$AsO compounds.

Fig 2: Temperature variation of magnetic susceptibility $M(T)$ in FC and ZFC condition for studied SmFe$_{0.9}$Co$_{0.1}$AsO. Inset shows the isothermal magnetization at different temperature for the same.

Fig 3: Complete magnetization loops $M(H)$ at 2 and 5K for studied SmFe$_{0.9}$Co$_{0.1}$AsO.

Fig. 4 Isothermal magnetization plots $M(H)$ at 50 and 100K for the studied SmFe$_{0.9}$Co$_{0.1}$AsO, the inset shows the $M(T)$ for the same in temperature range of 50 to 250K at 2.5 KOe applied field.
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Figure 1.

![Graph showing X-ray diffraction patterns for SmFe$_{0.9}$Co$_{0.1}$AsO and SmFeAsO.](image)

- **SmFe$_{0.9}$Co$_{0.1}$AsO**
  - $a = 3.9398(7)$ Å
  - $c = 8.4639(4)$ Å

- **SmFeAsO**
  - $a = 3.9375(6)$ Å
  - $c = 8.5021(4)$ Å
Figure 2.

The figure shows the magnetization ($M$ in emu/g) as a function of temperature ($T$ in K) for $\text{SmFe}_{0.9}\text{Co}_{0.1}\text{AsO}$ with an applied field ($H$) of 10 Oe. The graph includes two branches: FC (field-cooled) and ZFC (zero-field-cooled). The inset highlights the magnetization behavior at different temperatures: 9K, 7K, 5K, and 2K. The T$_C^{\text{dia}}$ = 14 K indicates the Curie temperature for the diamagnetic transition.
Figure 3.
Figure 4

The graph shows the magnetic moment (M) in emu/g as a function of the magnetic field (H) in KOe. The data is presented for two different temperatures: T = 100K (stars) and T = 50K (circles). The inset graph focuses on the SmFe$_{0.9}$Co$_{0.1}$AsO sample with a magnetic field of 2.5 KOe.

- **SmFe$_{0.9}$Co$_{0.1}$AsO**: The main graph includes two curves for different temperatures.
- **Inset**: A zoomed-in view of the SmFe$_{0.9}$Co$_{0.1}$AsO sample at H = 2.5 KOe.