

## Ir Doping-Induced Superconductivity in the SmFeAsO System

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Received February 10, 2009; E-mail: yzhao@swjtu.edu.cn

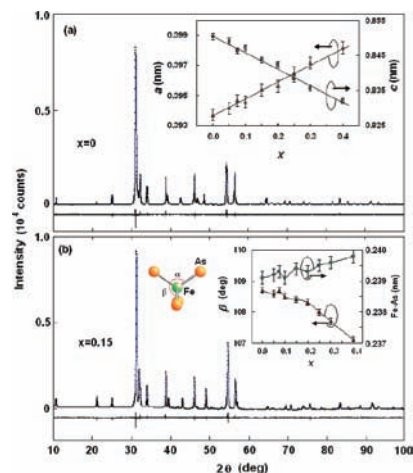
The discovery of superconductivity with  $T_c = 26$  K in F-doped LaFeAsO<sup>1</sup> has led to syntheses of a series of new FeAs-based superconductors, such as F-doped REFeAsO (RE = rare-earth)<sup>2–8</sup> and K-doped AFe<sub>2</sub>As<sub>2</sub> (A = alkaline-earth).<sup>9–11</sup> The highest  $T_c$  achieved to date is 56 K in Th-doped GdFeAsO.<sup>8</sup> The crystal structure of this new system is composed of a stack of alternating REO (or A) and FeAs layers in which the FeAs layers take responsibility for superconductivity whereas the REO (or A) layers act as charge reservoirs. Such a sandwich structure is very similar to that of the high- $T_c$  cuprates. However, in contrast to the cuprates, in which charge carriers must be introduced into the system through chemical doping in the charge-reservoir layers, in the FeAs-based compounds electrons can be directly doped into the conduction layers by partially replacing Fe with Co or Ni.<sup>12–15</sup> This has led to the discovery of new superconductors such as LaFe<sub>1-x</sub>Co<sub>x</sub>AsO,<sup>12</sup> BaFe<sub>2-x</sub>Co<sub>x</sub>As,<sup>13</sup> SmFe<sub>1-x</sub>Co<sub>x</sub>AsO,<sup>14</sup> etc.

Although different 3d transition metals, such as Cr, Mn, Co, Ni, Cu, etc., have been studied as dopants for Fe in the FeAs-based compounds,<sup>15</sup> only Co and Ni are able to induce superconductivity. Therefore, it would be interesting to know whether other transition metals, especially 5d transition metals, which are usually nonmagnetic, can induce superconductivity when they are doped for Fe in the FeAs-based compounds. Here we report that the Ir-doped SmFeAsO system is a new superconductor with  $T_c = 16$  K. In contrast to the Co-doping effect, which reduces the length of only the  $c$  axis while keeping the  $a$  axis nearly unchanged in the FeAs-based compounds, Ir doping in SmFeAsO significantly lengthens the  $a$  axis while reducing the length of the  $c$  axis.

Polycrystalline samples with a nominal composition of SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO were prepared by a solid-state reaction of SmAs (99.9%), Fe (99.99%), Ir (99.99%), and Fe<sub>2</sub>O<sub>3</sub> (99.9%). SmAs was obtained by reacting Sm pieces and As powders at 500 °C for 15 h and then 900 °C for 12 h. Powders of the raw materials were mixed well and then pressed into pellets in an inert atmosphere inside a glovebox. The pellets were wrapped with Ta foil, sealed in an evacuated quartz tube, and then annealed at 1150 °C for 36 h in an Ar atmosphere.

The crystal structure was studied by powder X-ray diffraction (XRD) using an X'Pert MRD diffractometer with Cu K $\alpha$  radiation. The samples in this study were pure phases, except for those with  $x = 0.14, 0.33, 0.4,$  and  $0.5$ , in which trace amounts of impurities were observed. Lattice constants and structure information were obtained from Rietveld refinements against the XRD data. The microstructure and composition of the sample were analyzed using scanning electron microscope (Quanta 200, FEI) equipped with an energy-dispersive spectroscopy (EDS) instrument. All of the samples showed a uniform microstructure and composition distribution. The Ir doping concentration was found to be close to the nominal one. DC magnetization was measured with a SQUID magne-

tometer (MPMS, Quantum Design), and resistivity measurements were performed with a physical property measurement system (PPMS, Quantum Design).



**Figure 1.** Powder XRD patterns of SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO (+) and Rietveld fits (solid lines) for (a)  $x = 0$  and (b)  $x = 0.15$ . The insets show (a) the lattice constants  $a$  and  $c$  and (b) the Fe–As bond length and As–Fe–As bond angle,  $\beta$ , vs Ir content,  $x$ .

Typical X-ray diffraction patterns for SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO with Rietveld fits are displayed in Figure 1. All of the samples show a tetragonal ZrCuSiAs-type structure, with lattice constants  $a = 0.3936(9)$  nm and  $c = 0.8503(7)$  nm for the undoped SmFeAsO sample. A clear shrinkage of the lattice constant  $c$  with increasing Ir content was observed. Meanwhile, the lattice constant  $a$  increased (Figure 1a, inset). The shrinkage of  $c$  is very similar to that observed in the Co-doped FeAs-based compounds. For example, at a doping level of 10 atom %,  $\Delta c/c$  (where  $\Delta c$  is the change in the lattice constant  $c$ ;  $\Delta a$  is defined similarly) is about  $-0.55\%$  for the present system, which is close to the values of  $-0.4\%$  for Co-doped BaFe<sub>2</sub>As<sub>2</sub><sup>13</sup> and  $-0.5\%$  for Co-doped CaFeAsF.<sup>16</sup> However, the significant increase in  $a$  ( $\Delta a/a = 0.23\%$ ) contrasts sharply with the values of 0.01 and 0.08% for Co-doped BaFe<sub>2</sub>As<sub>2</sub> and CaFeAsF, respectively.<sup>13,16</sup> Detailed structure information obtained from Rietveld refinements shows that Fe–As bond length in the FeAs layers is slightly stretched by Ir doping, but at the same time, the As–Fe–As bond angle,  $\beta$ , in the FeAs<sub>4</sub> tetrahedral clusters decreases (Figure 1b, inset), which contributes significantly to the increase in  $a$ . The change in  $\beta$  seen here is different from that for systems with doping of the charge reservoir layers (REO layers), where  $\beta$  increases with doping level.<sup>17</sup> Further work is required to fully explore the mechanisms behind this difference.

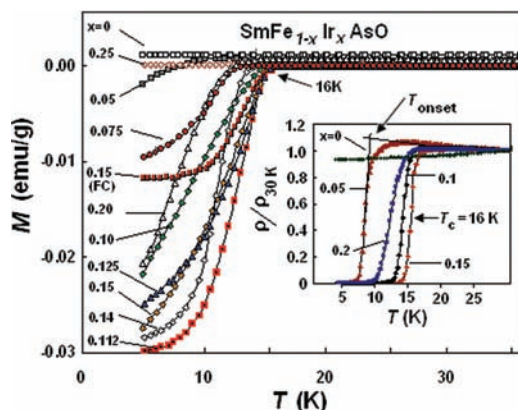
Figure 2 shows the temperature dependence of the dc magnetization,  $M$ , for SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO samples in a magnetic field of 10 Oe in zero-field-cooling (ZFC) mode. To demonstrate the bulk superconductivity,

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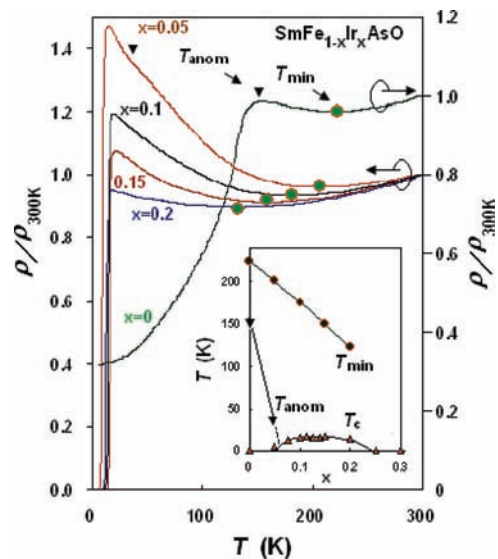
the sample with  $x = 0.15$  was also measured in field-cooling (FC) mode. The undoped SmFeAsO is nonsuperconducting down to 5 K, as expected. The sample with  $x = 0.05$  begins to show a superconducting transition at  $\sim 8$  K. The superconductivity transition shifts to higher temperatures with increasing Ir content, reaching a maximum value of  $\sim 16$  K at  $x = 0.15$ . However, the superconductivity is gradually suppressed with further increases in Ir content and vanishes at  $x = 0.25$ . The bulk feature of the superconductivity is demonstrated by the very striking Meissner effect for the  $x = 0.15$  sample in the dc magnetization measured in FC mode. The volume fraction of the superconducting phase estimated from the susceptibility is  $\sim 60\%$  at 5 K.



**Figure 2.** Temperature dependence of the dc magnetization for SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO samples measured at 10 Oe in ZFC mode. The data obtained in FC mode is also presented for the  $x = 0.15$  sample to demonstrate the Meissner effect. The superconducting transition can be seen in the samples with  $0.05 \leq x \leq 0.2$ . The inset shows the resistive transition for typical samples. The resistivity,  $\rho$ , is normalized to its value at 30 K. The determination of  $T_c$  and  $T_{\text{onset}}$  is illustrated.

The superconductivity of the SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO system is further confirmed by the temperature dependence of the resistivity,  $\rho$ , as shown in inset of Figure 2. For the  $x = 0.15$  sample, the value of  $T_c$  [defined as the temperature where the value of  $\rho$  decreases to half that at the onset transition temperature ( $T_{\text{onset}} = 17.3$  K)] is 16 K, which is slightly higher than those of Co-doped LaFeAsO (13 K)<sup>12</sup> and SmFeAsO (15 K).<sup>14</sup>

Besides the superconducting transition, the SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO system also shows a resistive anomaly, as observed in other FeAs-based compounds.<sup>1-11</sup>



**Figure 3.**  $\rho$ - $T$  plot for SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO samples, in which  $\rho$  is normalized to its value at 300 K. The inset shows  $T_c$ ,  $T_{\text{anom}}$ , and  $T_{\text{min}}$  as functions of Ir content.

As shown in Figure 3, the anomaly at  $T_{\text{anom}} = 155$  K in the undoped sample is significantly suppressed by Ir doping.  $T_{\text{anom}}$  drops to 36 K at  $x = 0.05$  and totally vanishes for  $x \geq 0.1$ .  $T_{\text{min}}$  is also observed to exist in the  $\rho$ - $T$  curves for all of the samples with  $x < 0.25$ , which is a peculiar feature for this type of high-temperature superconductor. The inset of Figure 3 summarizes  $T_{\text{anom}}$ ,  $T_{\text{min}}$ , and  $T_c$  as functions of  $x$ , demonstrating the phase diagram of the SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO superconducting system. It is worth noting that the phase diagram of the SmFe<sub>1-x</sub>Ir<sub>x</sub>AsO superconducting system is very similar to those of Co-doped FeAs-based compounds,<sup>16</sup> although Ir is a nonmagnetic 5d transition metal. The results indicate an alternative route to search for new superconductors in the FeAs-based compounds through chemical doping at the Fe site with a wide range of elements.

In summary, the electrical conductivity and magnetization measurements demonstrate that Ir doping is effective in inducing superconductivity in SmFeAsO by partially replacing Fe. The  $T_c$  value changes with Ir doping level, reaching a maximum value of 16 K at  $\sim 15$  atom %. Ir doping decreases the As-Fe-As bond angle,  $\beta$ ; this behavior is different from the change in  $\beta$  for the system with doping charges in the charge-reservoir layers.

**Acknowledgment.** The authors are grateful for the financial support of the National Natural Science Foundation of China under Grant 50588201, the National Basic Research Program of China (Program 973 under Grant 2007CB616906), the PCSIRT of the Ministry of Education of China (IRT0751), and the Australian Research Council under Grants DP0559872 and DP0881739. Y. L. Chen and Y. Zhang are also grateful for financial support from the Innovation Fund for Ph.D. Students of Southwest Jiaotong University.

**Supporting Information Available:** Microstructure, EDX analyses, powder XRD patterns, and structure information from Rietveld refinements against the XRD data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. *J. Am. Chem. Soc.* **2008**, *130*, 3296.
- (2) Takahashi, H.; Igawa, K.; Arii, K.; Kamihara, U.; Hirano, M.; Hosono, H. *Nature* **2008**, *453*, 376.
- (3) Chen, G. F.; Li, Z.; Wu, D.; Li, G.; Hu, W. Z.; Dong, J.; Zheng, P.; Luo, J. L.; Wang, N. L. *Phys. Rev. Lett.* **2008**, *100*, 247002.
- (4) Ren, Z.-A.; Yang, J.; Lu, W.; Yi, W.; Che, G.-C.; Dong, X.-L.; Sun, L.-L.; Zhao, Z.-X. *Mater. Res. Innovations* **2008**, *12*, 105.
- (5) Ren, Z.-A.; Yang, J.; Lu, W.; Yi, W.; Shen, Z.-L.; Li, Z.-C.; Che, G.-C.; Dong, X.-L.; Sun, L.-L.; Zhou, F.; Zhao, Z.-X. *Europhys. Lett.* **2008**, *82*, 57002.
- (6) Chen, X. H.; Wu, T.; Wu, G.; Liu, R. H.; Chen, H.; Fang, D. F. *Nature* **2008**, *453*, 761.
- (7) Ren, Z.-A.; Lu, W.; Yang, J.; Yi, W.; Shen, X.-L.; Li, Z.-C.; Che, G.-C.; Dong, X.-L.; Sun, L.-L.; Zhou, F.; Zhao, Z.-X. *Chin. Phys. Lett.* **2008**, *25*, 2215.
- (8) Wang, C.; Li, L.; Chi, S.; Zhu, Z.; Ren, Z.; Li, Y.; Wang, Y.; Lin, Z.; Luo, Y.; Jiang, S.; Xu, X.; Cao, G.; Xu, Z. *Europhys. Lett.* **2008**, *83*, 67006.
- (9) Rotter, M.; Tegel, M.; Johrendt, D. *Phys. Rev. Lett.* **2008**, *101*, 107006.
- (10) Chen, G. F.; Li, Z.; Li, G.; Hu, W. Z.; Dong, J.; Zhang, X. D.; Zheng, P.; Wang, N. L.; Luo, J. L. *Chin. Phys. Lett.* **2008**, *25*, 3403.
- (11) Wu, G.; Chen, H.; Wu, T.; Xie, Y. L.; Yan, Y. J.; Liu, R. H.; Wang, X. F.; Ying, J. J.; Chen, X. H. *J. Phys.: Condens. Matter* **2008**, *20*, 422201.
- (12) Sefat, A. S.; Huq, A.; McGuire, M. A.; Jin, R.; Sales, B. C.; Mandrus, D. *Phys. Rev. B* **2008**, *78*, 104505.
- (13) Sefat, A. S.; Jin, R.; McGuire, M. A.; Sales, B. C.; Singh, D. J.; Mandrus, D. *Phys. Rev. Lett.* **2008**, *101*, 117004.
- (14) Qi, Y.-P.; Gao, Z.-S.; Wang, L.; Wang, D.-L.; Zhang, X.-Z.; Ma, Y.-W. *Supercond. Sci. Technol.* **2008**, *21*, 115016.
- (15) Matsushita, S.; Inoue, Y.; Nomura, T.; Kamihara, Y.; Hirano, M.; Hosono, H. *New J. Phys.* **2009**, *11*, 025012.
- (16) Matsushita, S.; Inoue, Y.; Nomura, T.; Yanagi, H.; Hirano, M.; Hosono, H. *J. Am. Chem. Soc.* **2008**, *130*, 14428.
- (17) Lee, C. H.; Iyo, A.; Eisaki, H.; Kito, H.; Fernandez-Diaz, M. T.; Ito, T.; Kihou, K.; Matsuhata, H.; Braden, M.; Yamada, K. *J. Phys. Soc. Jpn.* **2008**, *77*, 083704.

JA901065P