Superconductivity above 50 K in Tb$_{1-x}$Th$_x$FeAsO

Lin-Jun Li, Yu-Ke Li, Zhi Ren, Yong-Kang Luo, Xiao Lin, Mi He, Qian Tao, Zeng-Wei Zhu, Guang-Han Cao$^*$ and Zhu-An Xu$^†$

Department of Physics, Zhejiang University, Hangzhou 310027, People’s Republic of China

We have successfully synthesized one member of LnFeAsO (Ln stands for lanthanides) with Ln=Tb. By partial substitution of Tb$^{3+}$ by Th$^{4+}$, superconductivity with onset $T_c$ up to 52 K was observed. In the undoped parent compound, the magnetic moments of Tb$^{3+}$ ions order antiferromagnetically (AFM) at $T_N$ of 2.5 K, and there exists an anomaly in the resistivity at $T^*$ of about 124 K which corresponds to the structural phase transition and/or AFM ordering of magnetic moments of Fe$^{2+}$ ions. This anomaly is severely suppressed by Th doping, similar to the cases of F doped LnFeAsO series. Thermopower measurements show that the charge carrier is electron-like for both undoped and Th doped compounds, and enhanced thermopower in Th doped samples was observed.

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The discovery of superconductivity at 26 K in LaFeAsO$_{1-x}$F$_x$ has led to a type of high temperature superconductors containing FeAs layers. The fluorine-doped family includes CeFeAsO$_{1-x}$F$_x$ (T$_c$ = 41 K), PrFeAsO$_{1-x}$F$_x$ (T$_c$ = 52 K), NdFeAsO$_{1-x}$F$_x$ (T$_c$ = 52 K), SmFeAsO$_{1-x}$F$_x$ (T$_c$ = 55 K) and GdFeAsO$_{1-x}$F$_x$ (T$_c$ = 36 K) in addition to LaFeAsO$_{1-x}$F$_x$. By using high-pressure synthesis method, a family of oxygen-deficient superconductors Fe$_x$As$_{1-x}$ (R=La, Ce, Pr, Nd and Sm) and GdFeAsO$_{1-x}$ were discovered. Through the Th$^{4+}$ substitution at the lanthanide site in GdFeAsO, we have recently obtained Gd$_{1-x}$Th$_x$FeAsO superconductors with $T_c$ up to 52 K.

The parent compounds of these superconductors have the general formula LnFeAsO (Ln=lanthanide), whose structure can be described as the stacking of alternative [Ln$_2$O$_2$]$^{2+}$ layers and [Fe$_2$As$_2$]$^{2-}$ layers. The [Ln$_2$O$_2$]$^{2+}$ layers act as a charge reservoir while the [Fe$_2$As$_2$]$^{2-}$ layers are superconductively active. Heterovalent substitutions of F$^-$ for O$^{2-}$ at the oxygen site or Th$^{4+}$ for Ln$^{3+}$ at the lanthanide site in the [Ln$_2$O$_2$]$^{2+}$ layers inject electrons onto [Fe$_2$As$_2$]$^{2-}$ layers, which results in the occurrence of superconductivity. Unfortunately, the parent compounds LnFeAsO were limited to Ln=La, Ce, Pr, Nd, Sm and Gd in the literatures. The LnFeAsO family member with Ln=Tb was mentioned as ternary TbFeAsO, but it was not reproduced as quaternary arsenide oxides later. Very recently a synthesis of TbFeAsO by high pressure reaction has been reported and superconductivity with $T_c$ of 46 K has been observed in F-doped TbFeAsO. However, there are few reports on the physical properties of this member probably due to the difficulty in obtaining single phase samples with high purity. In this paper, we report the synthesis of highly pure single phase TbFeAsO and the occurrence of superconductivity with $T_c$ as high as 52 K induced by the partial substitution of Tb$^{3+}$ by Th$^{4+}$. The magnetic properties of undoped TbFeAsO were also investigated. Th doping also induces enhanced thermopower in the normal state, which implies strong electron correlation in this system.

Polycrystalline samples of Tb$_{1-x}$Th$_x$FeAsO ($x=0, 0.1, 0.2$) were synthesized by solid state reaction in an evacuated quartz tube. The starting materials are Tb, Tb$_2$O$_7$, Th$_2$O$_3$, and As, which are all with high purity ($\geq 99.95$%). First, TbAs was presynthesized by reacting Tb tapes with As powders at 853 K for 10 hours and then 1173 K for 15 hours. Similarly, FeAs was prepared by reacting Fe with As powders at 853 K for 6 hours and then 1030 K for 12 hours. Then, the powders of TbAs, Tb$_2$O$_7$, Th$_2$O$_3$, Fe and As were weighed according to the stoichiometric ratio of Tb$_{1-x}$Th$_x$FeAsO. The weighed powders were mixed thoroughly by grinding, and pressed into pellets under a pressure of 200 MPa in an argon-filled glove box. The pressed pellets were wrapped with Ta foil, and sealed in an evacuated quartz ampoule. The sealed ampoule was slowly heated to 1453 K and kept for 48 hours. Finally the samples were furnace-cooled to room temperature. During the sample preparation, special measures were taken to avoid possible exposure to the fine particles of Th-contaminated materials in the air.

Powder X-ray diffraction (XRD) was performed at room temperature using a D/Max-rA diffractometer with Cu-K$_\alpha$ radiation and a graphite monochromator. The XRD diffractometer system was calibrated using standard Si powders. Lattice parameters were refined by the least-squares fit using at least 20 XRD peaks. The electrical resistivity was measured with a standard four-probe method. The temperature dependence of dc magnetization was measured on a Quantum Design Magnetic Property Measurement System (MPMS-5). The applied field was 1000 Oe for the undoped parent TbFeAsO sample and 10 Oe for the superconducting samples.

Fig. 1 shows the XRD patterns of the Tb$_{1-x}$Th$_x$FeAsO ($x = 0, 0.1, 0.2$) samples. The XRD peaks of the parent compound ($x = 0$) can be

$^*$Electronic address: ghcao@zju.edu.cn

$^†$Electronic address: zhuan@zju.edu.cn
and/or antiferromagnetic (AFM) transition in LaFeAsO. This anomaly is associated with a structural transition of the parent compound. X-ray diffraction studies have revealed that the impurities from ThO₂ can be observed. The refined lattice parameters are a = 3.899(3) Å and c = 8.409(5) Å for x = 0, smaller than those of the neighbor member GdFeAsO in the LnFeAsO family. In the case of the Th-doped samples, small amount of ThO₂ impurity can be observed. The refined lattice constants are a = 3.8998(3) Å, c = 8.4090(6) Å and a = 3.9025(3) Å, c = 8.4131(6) Å for x = 0.1 and 0.2, respectively. Therefore, the lattice parameters increase monotonically with increasing x. Because the ionic size of Th⁴⁺ is larger than that of Tb³⁺, the above result suggests the successful substitution of Tb³⁺ by Th⁴⁺. The incorporation of relatively large Th⁴⁺ ions can also relax the lattice mismatch between Ln₂O₃ fluorite-type block layers and Fe₃As₂ conducting layers.

The temperature dependence of the resistivity for the undoped parent compound (x=0) is shown in the upper panel of Fig. 2, and the magnetic susceptibility is also shown in the lower panel. Obviously the resistivity of the parent compound undergoes a sharp decrease below T* of 124 K, where T* is defined as the peak position in the curve of the derivative of resistivity versus temperature (shown in the inset of upper panel). Such an anomaly in the resistivity was also observed in the other LnFeAsO parent compounds. Low temperature neutron and X-ray diffraction studies have demonstrated that this anomaly is associated with a structural transition and/or antiferromagnetic (AFM) transition in LaFeAsO. However, T* is a little lower compared to the neighboring member GdFeOAs. We suggest that the decrease in T* could be correlated to the decrease in the radius of Ln³⁺ ions in the LnFeAsO parent compounds. The magnetic susceptibility shows good Curie-Weiss behavior and a drop in susceptibility appears around 2.5 K. Such a drop should be ascribed to AFM ordering of the magnetic moments of Tb³⁺ ions. It should be noted that there is a decreasing tendency in Tₓ as Ln goes from the light rare earth element (i.e. Sm) to heavy one. The effective magnetic moment is about 9.74 µB estimated from the fitting parameters with the Curie-Weiss formula, which is close to the magnetic moment (9.72 µB) of free Tb³⁺ ions.

The change of resistivity with Th doping is shown in Fig. 3. Upon Th doping, the resistivity anomaly around T* becomes less prominent and superconductivity occurs. The onset transition temperatures Tc (defined as the onset point in the resistive transition) are 45 K and 52 K for x = 0.1 and 0.2, respectively. Similar to the F-doped superconductors like LaFeAsO₁₋ₓFₓ, there is a kink in the resistivity above Tc in the "underdoped" region. Even for the x = 0.2 case, a kink is still observed around 120 K. The inset of Fig. 3 shows the dc magnetic susceptibility (χ) versus temperature for the x = 0.2 sample measured under zero-field cooling (ZFC) condition and H = 10 Oe. A clear superconducting transition begins at 52 K, consistent with the resistivity measurement. The magnetic

FIG. 1: (Color Online) Powder XRD patterns of Tb₁₋ₓThₓFeAsO (x=0, 0.1, 0.2) samples. The asterisks mark the impurities from ThO₂.

FIG. 2: (Color Online) Upper Panel: Temperature dependence of electrical resistivity for undoped TbFeAsO samples. The inset shows the derivative of resistivity as a function of temperature; Lower Panel: Temperature dependence of the magnetic susceptibility measured under H = 1000 Oe. The inverse of the magnetic susceptibility versus temperature is also shown to indicate the Curie-Weiss behavior. The inset shows the enlarged plot at low temperatures.
shielding fraction according to the ZFC susceptibility is above 50 % at $T = 4$ K. This implies bulk superconductivity induced by Th doping. The reduced magnetic shielding fraction is often observed in the poly-crystalline samples\(^3\) and it could be due to the granular property of the samples and existence of a few insulating impurities. The inhomogeneity of Th doping in the samples could also broaden the superconducting transition.

Fig. 4 shows the temperature dependence of thermopower for the $\text{Tb}_{1-x}\text{Th}_x\text{FeAsO} (x = 0, 0.1, 0.2)$ samples. All of the thermopower are negative at room temperature, which means that the electron-like charge carriers dominate. For the undoped parent compound, thermopower starts to increase abnormally from negative to positive below $T^\ast$. Similar anomalous increase in the thermopower below $T^\ast$ is also observed in the undoped $\text{LaFeAsO}^{10}$. This implies that the electronic state undergoes a severe change after the structural phase transition. Such an anomaly is completely suppressed in the Th doped samples. The thermopower drops to zero quickly below the superconducting transition temperature. The fact that both the anomaly in the resistivity and that in the thermopower are severely suppressed by Th doping indicates that superconductivity occurs as the AFM order is suppressed, which implies that superconductivity and AFM order are competing ground states in this system. To our surprise, the absolute value of thermopower, $|S|$, increases quickly with Th doping, and the maximum in $|S|$ is about 108 $\mu$V/K for $x = 0.2$, which is even comparable to that of the famous cobaltate $\text{Na}_x\text{CoO}_2$.\(^{22}\) It has been proposed that the doped iron-oxypnictides can be promising thermoelectric materials in refrigeration applications around liquid nitrogen temperatures.\(^{23}\) A rough estimate of $|S|$ according to the Mott expression gives a value of less than 10 $\mu$V/K for F doped LnFeAsO.\(^{22}\) More than 10 times enhanced value of $|S|$ strongly suggest that the electron correlation is very important in the Fe-based oxypnictide superconductors.

In summary, we have successfully synthesized one member of LnFeAsO family, TbFeOAs, without applying high pressure. By partial substitution of Tb\(^{3+}\) by Th\(^{4+}\), bulk superconductivity with onset $T_c$ up to 52 K is induced. The magnetic moments of Tb\(^{3+}\) ions antiferromagnetically (AFM) order at $T_N$ of 2.5 K in the parent compound. The anomaly in the resistivity corresponding to the structural phase transition and/or AFM ordering of magnetic moments of Fe\(^{2+}\) ions is suppressed by Th doping, which means that superconducting order and AFM order are competing orders in this system. Furthermore, the absolute value of thermopower increases abnormally with Th doping, implying strong correlation between electrons in this system.

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