

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

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We have successfully synthesized one member of LnFeAsO (Ln stands for lanthanides) with $\text{Ln}=\text{Tb}$. 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 electronlike 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 $\text{LaFeAsO}_{1-x}\text{F}_x$ (Ref. 1) has led to a type of high-temperature superconductors containing FeAs layers. The fluorine-doped family includes $\text{CeFeAsO}_{1-x}\text{F}_x$ ($T_c=41$ K),² $\text{PrFeAsO}_{1-x}\text{F}_x$ ($T_c=52$ K),³ $\text{NdFeAsO}_{1-x}\text{F}_x$ ($T_c=52$ K),⁴ $\text{SmFeAsO}_{1-x}\text{F}_x$ ($T_c=55$ K),⁵⁻⁷ and $\text{GdFeAsO}_{1-x}\text{F}_x$ ($T_c=36$ K),^{8,9} in addition to $\text{LaFeAsO}_{1-x}\text{F}_x$. By using a high-pressure synthesis method, a family of oxygen-deficient superconductors $R\text{FeAsO}_{1-x}$ ($R=\text{La, Ce, Pr, Nd, and Sm}$) (Ref. 10) and GdFeAsO_{1-x} (Ref. 11) was discovered. Through the Th^{4+} substitution at the lanthanide site in GdFeAsO , we have recently obtained $\text{Gd}_{1-x}\text{Th}_x\text{FeAsO}$ superconductors with T_c up to 56 K.¹²

The parent compounds of these superconductors have the general formula LnFeAsO ($\text{Ln}=\text{lanthanide}$),¹³ whose structure can be described as the stacking of alternative $[\text{Ln}_2\text{O}_2]^{2+}$ layers and $[\text{Fe}_2\text{As}_2]^{2-}$ layers. The $[\text{Ln}_2\text{O}_2]^{2+}$ layers act as a charge reservoir while the $[\text{Fe}_2\text{As}_2]^{2-}$ 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 $[\text{Ln}_2\text{O}_2]^{2+}$ layers inject electrons onto $[\text{Fe}_2\text{As}_2]^{2-}$ layers, which results in the occurrence of superconductivity. Unfortunately, the parent compounds LnFeAsO were limited to $\text{Ln}=\text{La, Ce, Pr, Nd, Sm, and Gd}$ in the literature. The LnFeAsO family member with $\text{Ln}=\text{Tb}$ was mentioned as ternary “ TbFeAs ”,¹⁴ but it was not reproduced as quaternary arsenide oxides later.¹³ 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 .¹⁵ 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 Brief Report, 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 $\text{Tb}_{1-x}\text{Th}_x\text{FeAsO}$ ($x=0,0.1,0.2$) were synthesized by solid-state reaction in an evacuated quartz tube. The starting materials are Tb, Tb_4O_7 ,

ThO_2 , Fe, 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 h and then 1173 K for 15 h. Similarly, FeAs was prepared by reacting Fe with As powders at 853 K for 6 h and then 1030 K for 12 h. Then, the powders of TbAs , Tb_4O_7 , ThO_2 , Fe, and FeAs were weighed according to the stoichiometric ratio of $\text{Tb}_{1-x}\text{Th}_x\text{FeAsO}$. 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 h. 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 a 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.

Figure 1 shows the XRD patterns of the $\text{Tb}_{1-x}\text{Th}_x\text{FeAsO}$ ($x=0,0.1,0.2$) samples. The XRD peaks of the parent compound ($x=0$) can be well indexed based on the tetragonal ZrCuSiAs -type structure with the space group $P4/nmm$ and no obvious impurity phases were detected. The refined lattice parameters are $a=3.8994(3)$ Å and $c=8.4029(5)$ Å for $x=0$, smaller than those of the neighbor member GdFeAsO in the LnFeAsO family.¹² In the case of the Th-doped samples, a small amount of ThO_2 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 Th^{4+} is larger than that of Tb^{3+} ,¹⁶ the above result suggests the successful substitution of Tb^{3+} by Th^{4+} . The incorporation of

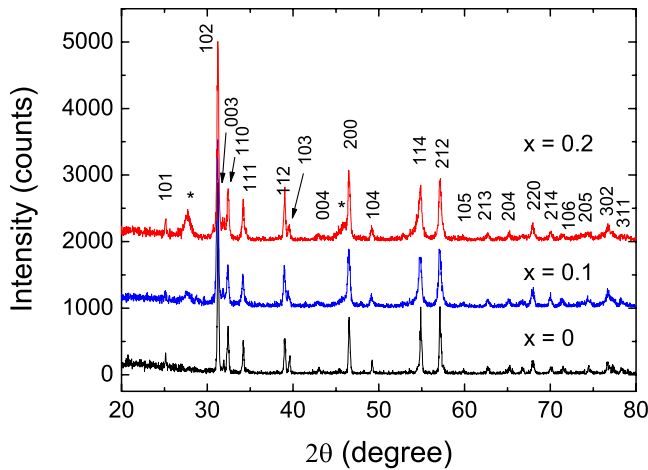


FIG. 1. (Color online) Powder XRD patterns of $\text{Tb}_{1-x}\text{Th}_x\text{FeAsO}$ ($x=0,0.1,0.2$) samples. The asterisks mark the impurities from ThO_2 .

relatively large Th^{4+} ions can also relax the lattice mismatch between Ln_2O_2 fluorite-type block layers and Fe_2As_2 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 com-

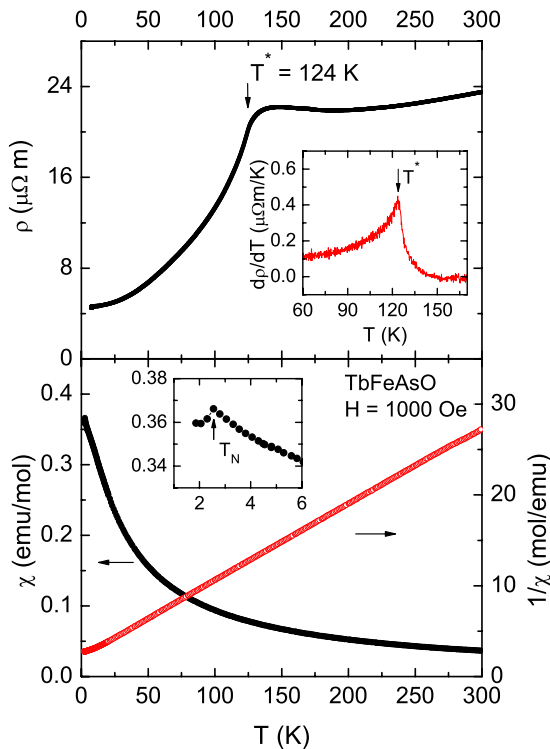


FIG. 2. (Color online) Upper panel: Temperature dependence of electrical resistivity for undoped TbFeAsO samples. Inset shows the derivative of resistivity as a function of temperature. Lower panel: Temperature dependence of the magnetic susceptibility measured under $H=1000$ Oe. The inverse of the magnetic susceptibility versus temperature is also shown to indicate the Curie-Weiss behavior. Inset shows the enlarged plot at low temperatures.

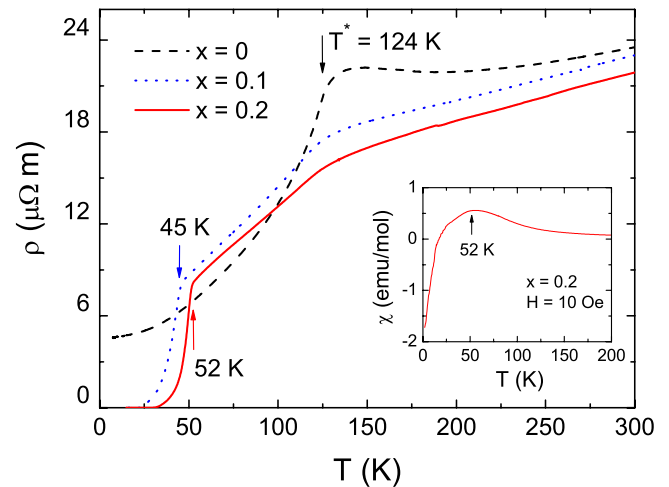


FIG. 3. (Color online) Temperature dependence of resistivity for $\text{Tb}_{1-x}\text{Th}_x\text{FeAsO}$ ($x=0,0.1,0.2$) samples. Inset shows the magnetic susceptibility measured under zero-field-cooling condition and $H=10$ Oe. Note that there exists a large contribution from the paramagnetic moments of Tb^{3+} in the normal state.

pound 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 the upper panel). Such an anomaly in the resistivity was also observed in the other LnFeAsO parent compounds.^{1,6,17} Low temperature neutron and x-ray diffraction studies^{18–20} 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 neighbor member GdFeAsO .¹² We suggest that the decrease in T^* could be correlated with the decrease in the radius of Ln^{3+} 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 Tb^{3+} ions. It should be noted that there is a decreasing tendency in T_N as Ln goes from the light rare-earth element (i.e., Sm) to the heavy one.^{12,21} The effective magnetic moment is about $9.74 \mu_B$ estimated from the fitting parameters with the Curie-Weiss formula, which is close to the magnetic moment ($9.72 \mu_B$) of free Tb^{3+} 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 T_c (defined as the onset point in the resistive transition) are 45 and 52 K for $x=0.1$ and 0.2, respectively. Similar to the F-doped superconductors such as $\text{LaFeAsO}_{1-x}\text{F}_x$, there is a kink in the resistivity above T_c 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 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

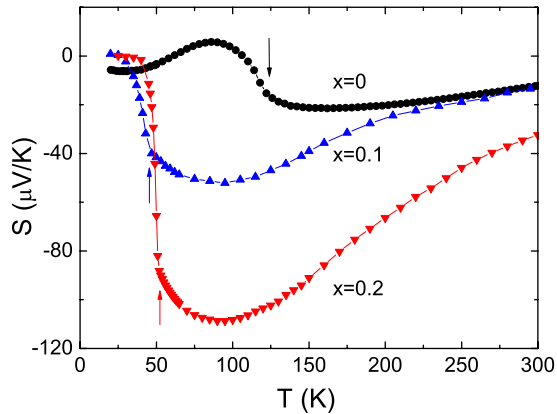


FIG. 4. (Color online) Temperature dependence of thermopower (S) for $\text{Tb}_{1-x}\text{Th}_x\text{FeAsO}$ ($x=0, 0.1, 0.2$) samples. The arrows indicate the position of T^* for $x=0$ and the positions of T_c for $x=0.1, 0.2$, respectively.

shielding fraction is often observed in the polycrystalline samples¹ 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.

Figure 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 is negative at room temperature, which means that the electronlike charge carriers dominate. For the undoped parent compound, the thermopower starts to increase abnormally from negative to positive below T^* . Similar anomalous increase in the thermopower below T^* is also observed in the undoped LaFeAsO .¹⁹ 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 two 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 $108 \mu\text{V}/\text{K}$ for $x=0.2$, which is even comparable to that of the famous cobaltate Na_xCoO_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 $10 \mu\text{V}/\text{K}$ for F-doped LnFeAsO .²⁴ The observed value of $|S|$ is more than 10 times enhanced, which strongly suggests that the electron correlation is very important in the Fe-based oxypnictide superconductors.

In summary, we have successfully synthesized one member of the LnFeAsO family, TbFeAsO , 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 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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