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Superconductivity at 43 K at ambient pressure in the iron-based layered compound $La_{1-x}Y_xFeAsO_y$

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Effect of Y substitution on the La-based iron oxypnictide superconductor $LaFeAsO_{0.6}$ is studied. Replacement of La^{3+} (1.16 Å) by smaller Y^{3+} (1.019 Å) in a form of $La_{1-x}Y_xFeAsO_{0.6}$ results in the decrease in lattice parameters, which likely causes pressure effect into the system. Superconducting transition temperature (T_c) increases monotonically with x, eventually up to 43.1 K for $x=0.5$. This T_c is comparable to the highest T_c reported for Y-free F-doped $LaFeAsO_{1-x}F_x$ under high pressure. The present results provide an alternative and much simpler way to achieve higher T_c in the La-based oxypnictide superconductors.

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The recent discovery of the Fe-based layered superconductor $LaFeAsO_{1-x}F_x$ with the transition temperature $T_c = 26$ K has sparked an intense research of the oxypnictides.[1] Shortly after the first report, replacement of La by other Ln elements (Ln=Sm, Ce, Nd, Pr, and Gd,) (Refs. 2–4) yields achievement of higher T_c (>50 K) in these compounds. Subsequently, F-free, O-deficient $LnFeAsO_{1-y}$ was reported to superconduct at almost the same T_c.[2,5] So far, attempts to raise T_c of the original superconductor, $LaFeAsO_{1-x}F_x$, have been made by applying external pressure,[6] resulting in the increase in T_c up to 43 K under the pressure of 4 GPa.

Substitution of smaller Ln ions, as well as application of external pressure, causes lattice shrinkage. It is therefore naturally expected that high T_c favors smaller lattice parameters. If this is really the case, one should be able to control (hopefully raise) T_c once one can develop a way to tune the lattice parameters. Here we report that the chemical substitution of La ions by smaller Y ions meets that purpose. In $La_{1-x}Y_xFeAsO_{1-\delta}$, T_c monotonically increases with x, up to 43.1 K for $x=0.5$. The present results provide an alternative and much easier way to increase T_c in the La-based oxypnictide superconductors.

Polycrystalline samples were prepared by high-pressure synthesis method using a cubic-anvil-type apparatus (Riken CAP-07). Powders of LaAs, YAs, Fe, and Fe_2O_3 were used as the starting materials. LaAs and YAs were synthesized by reacting La, Y, and As at 500 °C for 15 h and then 850 °C for 5 h in an evacuated quartz tube. The starting materials were mixed with nominal compositions of $La_{1-x}Y_xFeAsO_{0.6}$ ($x=0$, 0.1, 0.2, 0.3, 0.4, and 0.5) and ground by an agate mortar in a glove box filled with dry nitrogen gas. In the case of oxypnictide, boundary between superconducting state and nonsuperconducting one is clear with the variation in the oxygen content. When the a parameter is reduced by increasing oxygen deficiency, superconductivity is induced with an abrupt raise of T_c at a certain oxygen deficiency (lattice parameters) and the T_c saturates when oxygen content is lower than 0.65 in $LnFeAsO_{0.65}$. The nominal oxygen contents of the samples that are located at the boundary between superconducting and nonsuperconducting were about 0.8 for all the $LnFeAsO_{1-y}$ series. The T_c was less sensitive to the nominal oxygen content of the samples when the nominal oxygen content are around 0.6 for all the $LnFeAsO_{1-y}$ series. So we selected the oxygen content=0.6 in $La_{1-x}Y_xFeAsO_{0.6}$ ($x=0$, 0.1, 0.2, 0.3, 0.4, and 0.5). The samples were synthesized by heating the mixtures in boron nitride (BN) crucibles under a pressure of about 2 GPa at 1150 °C for 2 h. Powder x-ray diffraction (XRD) patterns were measured using CuK_a radiation (Rigaku RINT 1100). The lattice parameters were calculated by the least-square fit method. In order to characterize the superconducting properties, zero-field cooled (ZFC) (shielding signal) and field-cooled (FC) (Meissner signal) magnetization measurements were performed using a quantum design magnetic property measurement system (MPMS) magnetometer with an applied field of 5 Oe. The resistivity was measured by a standard four-probe method.

Figure 1 shows the powder XRD patterns of the samples with nominal compositions of $La_{1-x}Y_xFeAsO_{0.6}$ ($x=0$, 0.1, 0.2, 0.3, 0.4, and 0.5). The ZrCuSiAs-type crystal structure

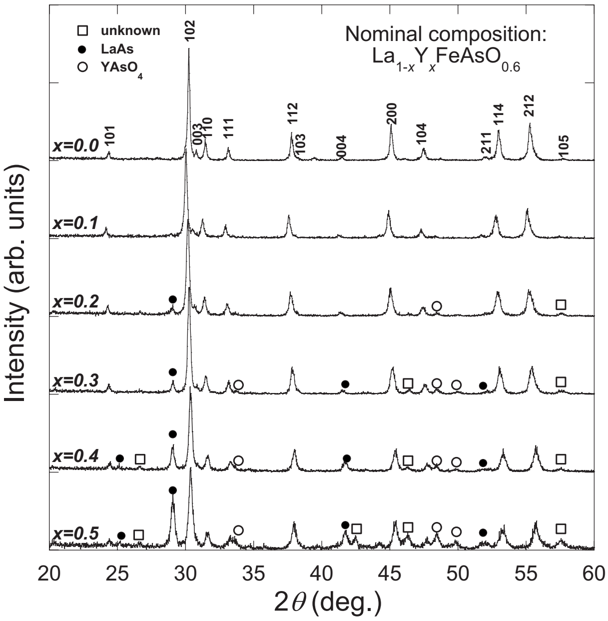

FIG. 1. Powder x-ray diffraction patterns of samples with nominal compositions of $La_{1-x}Y_xFeAsO_{0.6}$ ($x=0$, 0.1, 0.2, 0.3, 0.4, and 0.5). The impurity phases are indexed by open circles ($YAsO_4$), solid circles (LaAs), and open squares [unknown impurity phase(s)], respectively.

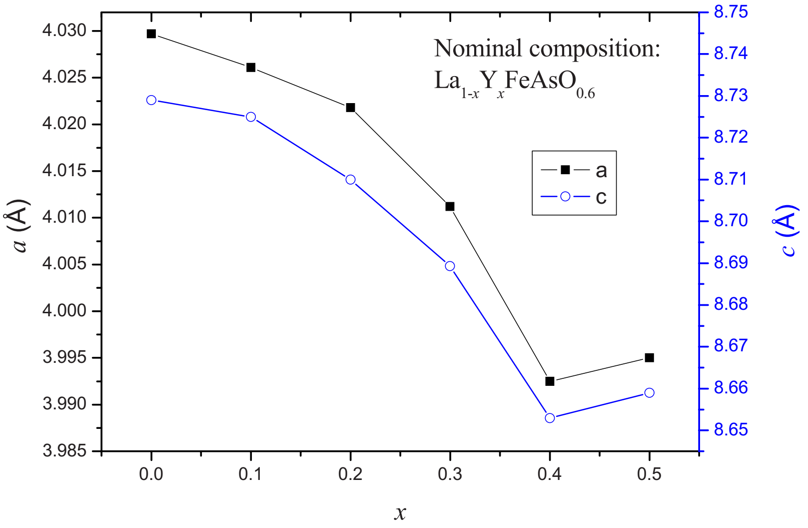

FIG. 2. (Color online) Variation in the lattice parameters as a function of x for $La_{1-x}Y_xFeAsO_{0.6}$.

($P4/nmm$), as expected for LaFeAsO (and its oxygen-deficient form), is formed as the main phase for all samples. For $x=0$ and 0.1, all the apparent peaks can be indexed based on the LaFeAsO-type[7] crystal structure. Peaks due to impurity phases [$YAsO_4$, LaAs, and unknown phase(s)] appear at $x=0.2$, which increase with increasing x. It is inevitable since $x=1$ compound, i.e., $YFeAsO_{1-\delta}$, does not exist and more Y tends to be expelled out of the samples with increasing x. Accordingly, the notation used in the paper simply means the nominal value of the sample composition and does not necessarily agree with the real composition.

Figure 2 shows the variation in the lattice parameters as a function of x. Overall, the lattice parameters shrink with increasing x both along a and c axes, which is reasonable because the ionic radius of Y^{3+} (1.019 Å) is smaller than that of La^{3+} (1.16 Å).[8] In comparison to $x=0$ ($a=4.029$ Å and $c=8.729$ Å), the a- and c-axis length for $x=0.4$ ($a=3.992$ Å and $c=8.652$ Å) shrinks by 0.92% and 0.88%, respectively. The change in the lattice parameters is significantly larger compared to the F-doped LaFeAsO,[1] in which the lattice parameters decreased only 0.2% (a axis) and 0.3% (c axis) by 8% F doping. The small increase in the lattice parameters at $x=0.5$ than $x=0.04$ may be due to solubility limit of Y at the La site, at present preparation conduction.

The temperature (T) dependence of the magnetic susceptibility (χ) of $La_{1-x}Y_xFeAsO_{0.6}$ is shown in Fig. 3. The clear drop in χ, corresponding to the onset of superconductivity (indicated by arrows), is observed for all samples. Here we adopt two definitions to determine T_c, as shown in the inset of Fig. 3. The first one is $T_c-\chi$(onset) defined as the temperature where χ starts to drop. The other, $T_c-\chi$(cross), is determined from the intersection of the two extrapolated lines: one is drawn through χ in the normal state just above T_c, and the other is drawn through the steepest part of χ in the superconducting state. As shown in detail later, $T_c-\chi$(onset) tends to be higher than $T_c-\chi$(cross) by 2–3 K. The volume fractions estimated from the magnitude of shielding signal at 5 K are in the order of 15%–61% for $x=0-0.5$. We note that the sample has large T-independent magnetic moment above T_c due to ferromagnetic impurities, most likely Fe_2O_3 and/or Fe.

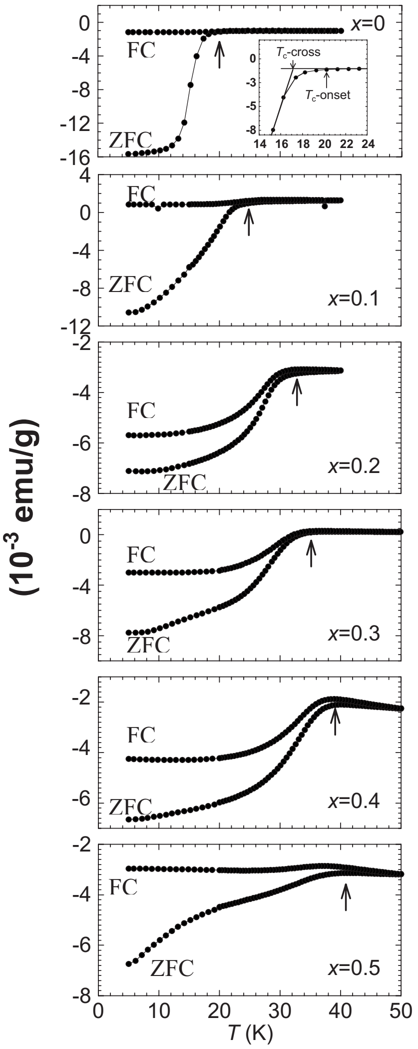

FIG. 3. Temperature dependence of magnetic susceptibility of $La_{1-x}Y_xFeAsO_{0.6}$ for $x=0-0.5$. The field cooled and zero-field cooled curves are represented by FC and ZFC, respectively. The onset in magnetic susceptibility (χ) is indicated by arrows.

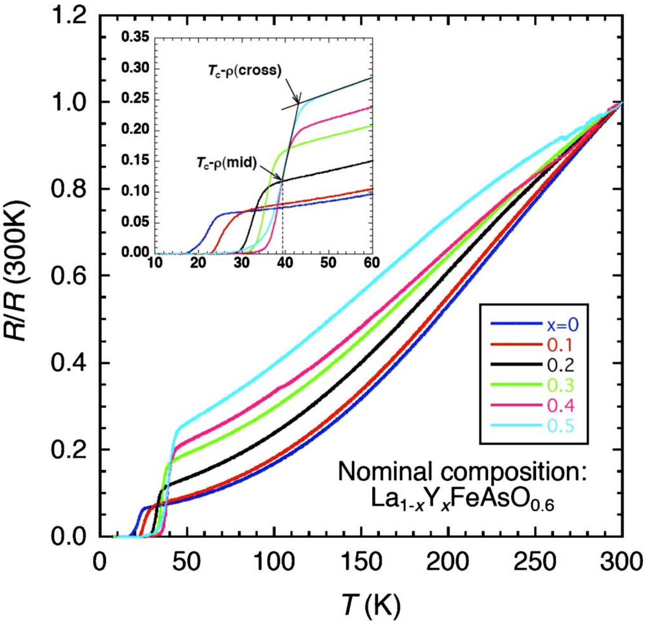

FIG. 4. (Color online) Temperature dependence of La$_{1-x}$Y$_x$FeAsO$_{0.6}$ resistivity for $y=0-0.5$.

Figure 4 shows temperature (T) dependence of the resistivity (ρ) (magnitude normalized at 300 K). The observed superconducting transition is rather broad, indicating the inhomogeneous distribution of T_c within samples. Accordingly, we employed three definitions for T_c (see inset of Fig. 4) as follows. (1) $T_c-\rho$(cross), determined from the intersection of the two lines: one is drawn through ρ in the normal state just above T_c, and the other is drawn through the steepest part of ρ in the superconducting state. Note that the 43 K value of LaFeAsO$_{1-x}$F$_x$ under high pressure is obtained using this definition. (2) $T_c-\rho$(mid), determined at the temperature where the resistivity is 50% of its value at the $T_c-\rho$(cross). (3) $T_c-\rho$(zero), the temperature where the resistivity becomes zero.

The x dependence of $T_c-\rho$(cross), $T_c-\rho$(mid), and $T_c-\rho$(zero), as well as $T_c-\chi$(onset) and $T_c-\chi$(cross), is summarized in Fig. 5. Regardless of the definition, T_c increases with increasing x except $T_c-\rho$(zero). In particular, $T_c-\rho$(cross) reaches 43.1 K at $x=0.5$, almost the same as the maximum $T_c-\rho$(onset) of F-doped LaFeAsO (Ref. 6) under pressure.

For all x's, the relationship

$$T_c-\rho(\text{zero}) \leq T_c-\chi(\text{cross}) < T_c-\chi(\text{onset})$$
$$= T_c-\rho(\text{mid}) < T_c-\rho(\text{cross})$$

is fulfilled. This is reasonable, considering that the present samples (and most of the existing samples in literatures which exhibit similar behaviors) are rather inhomogeneous and possess T_c distribution. In an inhomogeneous superconductor, ρ starts to drop at $T_c-\rho$(cross) when the highest T_c part of the sample becomes superconducting even though its volume fraction is below the detection limit of χ. With lowering T, the superconducting volume fraction increases, leading the drop in χ and (further) drop in ρ, marked as $T_c-\chi$(onset) and $T_c-\rho$(mid), respectively. $T_c-\chi$(cross) characterizes the average T_c of the sample. $T_c-\rho$(zero) is affected by some extrinsic factors, such as nonsuperconducting grain boundaries which terminate the supercurrents. Note that $x=0.5$ sample contains higher impurities and the T_c determined by χ should not be affected. If the above consideration holds, $T_c-\rho$(cross) indicates the potentially attainable T_c of the system which should be obtained in a single-phase form by optimizing the synthesis condition, while either $T_c-\chi$(cross) or $T_c-\chi$(onset) is more adequate as T_c of existing samples.

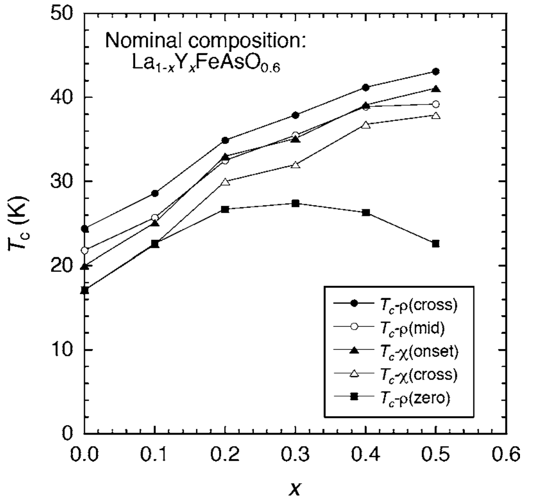

FIG. 5. x dependence of $T_c-\rho$(cross), $T_c-\rho$(mid), $T_c-\rho$(zero), $T_c-\chi$(onset), and $T_c-\chi$(cross).

The present results indicate that T_c increases and lattice parameters shrinks concomitantly with x. This fact strongly suggests that the inner chemical pressure caused by Y-La substitution is an important factor that improves T_c.[9] It is also consistent with the fact that materials containing smaller Ln ions tend to have higher T_c. To make the arguments more quantitative, we plot in Fig. 6 the a-axes parameter vs $T_c-\chi$(onset) of La$_{1-x}$Y$_x$FeAsO$_{0.6}$, together with those obtained for LnFeAsO$_{0.6}$ (Ln=La, Pr, Nd, Sm, and Gd) synthesized using the same method.[10] [T_c of the other LaFeAsO$_{0.6}$

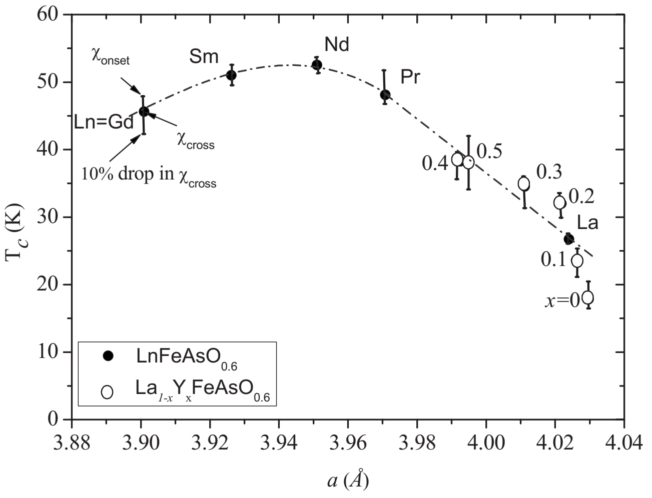

FIG. 6. Relationship between the a-axis parameter and $T_c-\chi$(cross) of La$_{1-x}$Y$_x$FeAsO$_{0.6}$ and LnFeAsO$_{0.6}$ (Ln=La, Pr, Nd, Sm, and Gd).

(black circle) is higher than that presented in this report, presumably due to the slight difference in oxygen content and/or the amount of impurity phase. However, the difference in T_c does not affect the discussion presented here.] We considered $T_c-\chi$(cross) as an average value of the T_c and plotted the T_c value determined from the susceptibility data as an error bar which is determined from the three different points from the susceptibility curves: $T_c-\chi$(onset), $T_c-\chi$(cross), and 10% drop in $T_c-\chi$(cross). We used $T_c-\chi$(onset) as the upper limit, $T_c-\chi$(cross) as an average T_c, and 10% drop in $T_c-\chi$(cross) [it is the value of T_c where the χ(cross) drops to 10% of its original value] as lower limit of T_c in the error bars.

Clearly, both for $LnFeAsO_{0.6}$ and $La_{1-x}Y_xFeAsO_{0.6}$, the *a* axis vs T_c relationship collapses into the same line, indicating that the T_c enhancement mechanism is the same. In particular, La-Y substitution allows one to continuously change T_c between 20 K to over 40 K by simply changing x.

Coming back to Fig. 4, one can see that the positive curvature, fitted in a form

$$\rho(T) = AT^{\alpha} + B, \quad \alpha > 1,$$

is observed above T_c up to 300 K in the T dependence of resistivity for $x=0$. This behavior is commonly observed for La-based oxypnictide superconductors, such as F-doped LaFeAsO.[1] Interestingly, with increasing x, the curvature changes to S shape, most prominent at $x=0.5$. The T dependence of resistivity is similar to other oxypnictide superconductors with higher T_c, such as $PrFeAsO_{1-x}F_x$, $SmFeAsO_{1-x}F_x$, $NdFeAsO_{1-x}F_x$, and $NdFeAsO_{0.6}$.[2,11] This systematic evolution of $\rho(T)$ behavior as a function of x can be also taken as an evidence that Y substitution in $LaFeAsO_{1-\delta}$ enhances the T_c value from (<30 K) to (>50 K) and that the present system is quite a suitable material to make clear the mechanism of highT_c in the oxypnictide superconductors.

In conclusion, we have successfully enhanced T_c of $LaFeAsO_{0.6}$, originally 20 K class superconductor, up to 43.1 K by replacing La^{3+} by smaller Y^{3+}. This T_c is comparable to the highest T_c reported for Y-free F-doped $LaFeAsO_{1-x}F_x$ under high pressure. The present results provide an alternative and much simpler way to achieve higher T_c in the La-based oxypnictide superconductors.

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