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Narrow superconducting window in LaFe$_{1-x}$Ni$_x$AsO

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We have studied Ni-substitution effect in LaFe$_{1-x}$Ni$_x$AsO ($0 \leq x \leq 0.1$) by the measurements of x-ray diffraction, electrical resistivity, magnetic susceptibility, and heat capacity. The nickel doping drastically suppresses the resistivity anomaly associated with spin-density-wave ordering in the parent compound. Superconductivity emerges in a narrow region of $0.03 \leq x \leq 0.06$ with the maximum $T_c$ of 6.5 K at $x = 0.04$, where enhanced magnetic susceptibility shows up. The upper critical field at zero temperature is estimated to exceed the Pauli paramagnetic limit. The much lowered $T_c$ in comparison with LaFeAsO$_{1-x}$F$_x$ system is discussed.

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I. INTRODUCTION

The discovery of superconductivity at 26 K in LaFeAsO$_{1-x}$F$_x$ (Ref. 1) and the subsequent findings of the enhanced superconductivity with $T_c$ up to 56 K (Refs. 2–5) in a series of iron-arsenides have stimulated enormous research interest. It has been suggested that both electronic correlations and multiorbital/band effects should play important roles.6–12 The prototype parent compound, LaFeAsO, undergoes a structural phase transition at 155 K,13,14 followed by a collinear antiferromagnetic (AFM) spin-density-wave (SDW) transition at lower temperature.13,15 Electron/hole doping into the FeAs layers suppresses the long-range SDW order, in favor of superconductivity.15,16 This phenomenon is apparently analogous to that in cuprates, where superconductivity is induced by doping of charge carriers into an AFM Mott insulator. The iron arsenides, however, also show remarkable differences from the cuprates. For example, the parent compounds of iron arsenides show itinerant character of Fe 3$d$ electrons,17–20 while Cu 3$d$ electrons in the parent compounds of the cuprates are localized.

As inferred in the band structure calculations for LaOMAs (M = Mn, Fe, Co, and Ni),21 Fe-site doping with Co or Ni in the parent compounds of iron arsenides may also introduce additional electrons, hence possibly inducing superconductivity. This has been experimentally realized for the Co doping with $T_c \sim 13$ K in LaFe$_{1-x}$Co$_x$AsO (Refs. 22 and 23) and $T_c = 22$ K in BaFe$_{1.8}$Co$_{0.2}$As$_2$.24 Since Ni atoms have one more electron than Co, one would expect that substitution of Fe with Ni introduces carriers more effectively. A possible hint comes from the Ni-based superconducting analog, LaNiAsO, which is a superconductor with $T_c \sim 2.5$ K.25,26 The normal state of the LaNiAsO superconductor is Pauli paramagnetic,26 suggesting that the Ni 3$d$ electrons have an itinerant character.

In this paper we report the realization of superconductivity in LaFe$_{1-x}$Ni$_x$AsO ($0 \leq x \leq 0.1$). Superconductivity has been observed in a narrow region of $0.03 \leq x \leq 0.06$ with a lowered maximum $T_c$ of 6.5 K. The optimal doping level is found to be about half of that in LaFe$_{1-x}$Co$_x$AsO (Ref. 23) system. The occurrence of superconductivity by Ni doping at Fe site contrasts sharply with severe suppression of superconductivity by the Cu-site doping with Ni in cuprate superconductors.

II. EXPERIMENTAL

Polycrystalline LaFe$_{1-x}$Ni$_x$AsO samples were synthesized by solid state reaction in vacuum, similar to previous report.23 Powders of LaAs, La$_2$O$_3$, FeAs, Fe$_2$As and NiO were weighed according to the stoichiometric ratios of LaFe$_{1-x}$Ni$_x$AsO ($x = 0$, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08, and 0.1), and thoroughly mixed in an agate mortar and pressed into pellets under a pressure of 2000 kg/cm$^2$. The pellets were sealed in evacuated quartz tubes, then heated uniformly at 1433 K for 48 h, and finally cooled by shutting off the furnace.

The resultant samples were characterized by powder x-ray diffraction (XRD) with Cu $K\alpha$ radiation. The XRD diffractometer system was calibrated using standard Si powders. The detailed structural parameters were obtained by Rietveld refinements, using the step-scan XRD data with $10^\circ \leq 2\theta \leq 120^\circ$. The typical $R$ values of the refinements are: $R_F \sim 2.8\%$, $R_I \sim 4.6\%$, and $R_w \sim 13\%$. The goodness-of-fit parameter, $S = R_w/R_{exp} \sim 1.6$, indicating good reliability of the refinement.

The electrical resistivity was measured with a standard four-terminal method. Samples were cut into a thin bar with typical size of $4 \times 2 \times 0.5$ mm$^3$. Gold wires were attached onto the samples’ abraded surface with silver paint. The size of the contact pads leads to a total uncertainty in the absolute values of resistivity of 10%. The measurements of magnetoresistance and heat capacity were carried out on a Quantum Design physical property measurement system (PPMS-9). Temperature dependence of magnetization was measured on a Quantum Design magnetic property measurement system (MPMS). In the measurements of normal-state susceptibility, the background data from the sample holder were removed. For the measurement of the superconducting (SC) transitions, both the zero-field cooling (ZFC) and field cooling (FC) protocols were employed under the field of 10 Oe.
III. RESULTS AND DISCUSSION

Figure 1(a) shows XRD patterns of the representative samples of LaFe_{1-x}Ni_{x}AsO. The XRD peaks are well indexed based on a tetragonal cell with the space group of P4/nmm, indicating that the samples are essentially single phase. The lattice parameters are plotted in the inset as functions of \( x \). With the increase in Ni doping, the \( a \) axis increases slightly, while the \( c \) axis shrinks remarkably. The cell volume is consequently decreased by the incorporation of Ni.

The crystallographic parameters were obtained by the Rietveld refinement [Fig. 1(b)] based on ZrCuSiAs-type structure. Table I compares the structural data of undoped and Ni-doped samples. The Ni doping enlarges the Fe-Fe spacing slightly, but compresses the FeAs layers significantly. In other word, the most remarkable effect of Ni doping on the crystal structure is that As atoms are pulled narrower if samples were homogeneous. Similar phenomena were also observed in LaFe_{1-x}Co_{x}AsO systems.

To verify bulk superconductivity further, we performed specific-heat (\( C \)) measurement for the sample of \( x=0.04 \). The result is shown in Fig. 4. A specific-heat anomaly can be seen at \( T_c \sim 6.5 \) K (a tiny anomaly at about 8 K might be related to the trace residual SDW transition). In the temperature range from 6.7 to 10 K, the specific heat can be well described by the sum of electronic and lattice contributions: \( C = \gamma T + \beta T^3 \). Therefore, the linear fit for \( C/T \) versus \( T^2 \) gives the electronic specific-heat coefficient \( \gamma = 5.74 \) mJ/(mol K^2) and the lattice specific-heat coefficient \( \beta = 0.254 \) mJ/(mol K^3). The Debye temperature \( \theta_D \) is then calculated to be 285 K, using the formula \( \theta_D = (12\pi Nk/\beta)^{1/3} \), where \( N \approx 4 \) and \( R = 8.314 \) J/(mol K). The value of \( \theta_D \) is close to that of LaFeAsO (282 K, Ref. 15) and that of LaFeAs_{0.83}Fe_{0.17} (308 K, Ref. 28). The value of \( \gamma \) is also comparable to those of LaFeAsO_{1-x}F_{x} samples (Refs. 15 and 28).

Table I. Crystallographic data of LaFe_{1-x}Ni_{x}AsO (\( x=0 \) and 0.04) at room temperature. The space group is \( P4/nmm \). The atomic coordinates are as follows: La (0.25, 0.25, z); FeNi (0.75, 0.25, 0.5); As (0.25, 0.25, z); O (0.75, 0.25, 0).

| Compounds          | LaFeAsO | LaFe_{0.98}Ni_{0.02}AsO |
|--------------------|---------|-------------------------|
| \( a (\text{Å}) \) | 4.0357(3)| 4.0376(3)               |
| \( c (\text{Å}) \) | 8.7378(6)| 8.7208(6)               |
| \( V (\text{Å}^3) \) | 142.31(2)| 142.17(2)               |
| \( z \) of La      | 0.1411(2)| 0.1422(2)               |
| \( z \) of As      | 0.6513(3)| 0.6505(3)               |
| FeAs-layer thickness (Å) | 2.644(2) | 2.624(2)               |
| Fe-Fe spacing (Å)  | 2.8536(3)| 2.8550(3)               |
| As-Fe-As angle (°) | 113.5(1) | 114.0(1)                |

Figure 3 shows SC diamagnetic transitions in LaFe_{1-x}Ni_{x}AsO. Although samples with \( x \leq 0.02 \) show no diamagnetic signal above 1.8 K, magnetic expelling/screening can be clearly seen for 0.03 \( \leq x \leq 0.06 \) at low temperatures. The magnetic shielding fraction of the sample of \( x=0.04 \) is estimated to be 45%, confirming bulk superconductivity. The diamagnetic curve shows steplike feature, probably due to sample inhomogeneity and/or an intergrain SC transition. The diamagnetic signal for other SC samples is much lower, implying that the SC region would be even narrower if samples were homogeneous. Similar phenomena were also observed in LaFe_{1-x}Co_{x}AsO systems.

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which leads to an estimated upper critical field at zero-field $H_{c2}$, $NARROW$ SUPERCONDUCTING WINDOW IN LaFe$_{1-x}$Ni$_x$AsO. Note that the open and filled symbols denote ZFC and FC data, respectively. The inset is an expanded plot for showing the data of $x=0.02, 0.06$ and 0.10.

After subtracting the lattice contribution to the specific heat, the specific-heat jump at the SC transition can be obviously seen, confirming bulk superconductivity. The dimensionless parameter $\Delta C_v/\gamma T$ at $T_c$ is estimated to be 0.73, much lower than the expected value of 1.43 for an isotropic SC gap. This observation is similar to that in Ni-doped samples. One may also see two transitions at 5 and 6.5 K, in accordance with the above steplike diamagnetic susceptibility curve. This phenomenon is probably due to the sample inhomogeneity and/or intergrain SC transition as mentioned above, however, the possibility of multiband superconductivity cannot be fully ruled out.

Figure 5 shows suppression of SC transition in resistivity under magnetic fields for the sample of $x=0.04$. The applied field shifts the SC transition toward lower temperatures, and the transition becomes broadened. The inset plots the temperature dependence of $T_c$ ($H$), defined as the temperature where the resistivity falls to one-half of the normal-state value. The initial slope $\mu_0\partial H_c^2/\partial T$ near $T_c$ is $-3.81$ T/K, which leads to an estimated upper critical field at zero-field $\mu_0H_c^2(0)\sim 17$ T using Werthamer-Helfand-Hohenberg model (Ref. 29). This value of upper critical field exceeds the Pauli paramagnetic limit $\mu_0H_p=1.84T_c\sim 12$ T (Ref. 30). Similar observations have been reported in LaFeAsO$_{1-x}$F$_x$ system. The high critical field makes LaFe$_{0.96}$Ni$_{0.04}$AsO fundamentally different from the LaFeNiO superconductor (Refs. 25 and 26).

The normal-state susceptibility $\chi$ of the Ni-doped samples is shown in Fig. 6. The $\chi(T)$ are characterized by linear decrease at high temperatures as well as Curie-like upturn below $\sim 100$ K. The Curie-like upturn was found to be sensitive to sample’s quality. Generally, better sample shows smaller susceptibility upturn. Thus, the susceptibility upturn is mainly due to an extrinsic origin (such as defects and trace impurities). The linear $T$-dependence of $\chi$ was experimentally demonstrated in LaFeAsO$_{1-x}$F$_x$ (Ref. 33) and BaFe$_2$As$_2$ (Ref. 34) systems, and was discussed in terms of the “preformed SDW moments”. The measured $\chi(T)$ can thus be fitted with the formula,

$$\chi(T) = \chi_0 + \alpha T + \frac{C}{T},$$

where the $T$-independent term $\chi_0$ contains Pauli paramagnetic susceptibility ($\chi_P$) (Ref. 36) from itinerant electrons...
and Larmor diamagnetic susceptibility ($\chi_{\text{core}}$) from ionic cores. It is noted that the change in $\chi_0$ with the Ni doping is primarily due to the variation of $\chi_p$.

To avoid the influence of the structural transition for $0 \leq x \leq 0.02$, we made the fitting using different range of data as follows: $160 \text{ K} \leq T \leq 300 \text{ K}$ for $x = 0$, $110 \text{ K} \leq T \leq 300 \text{ K}$ for $x = 0.01$, $75 \text{ K} \leq T \leq 300 \text{ K}$ for $x = 0.02$, $50 \text{ K} \leq T \leq 300 \text{ K}$ for $x = 0.03$, and $30 \text{ K} \leq T \leq 300 \text{ K}$ for $x > 0.03$. The fitted parameters are listed in Table II. It is shown that the $\alpha$ values are about $4 \times 10^{-7}$ emu mol$^{-1}$ K$^{-1}$, almost independent of Ni-doping $x$, similar to the case reported in LaFeAsO$_{1-x}$F$_x$. The extracted $\chi_0$, shown in the inset of Fig. 6, tends to decrease with increasing Ni-doping, with an enhancement in the SC regions centered at $x = 0.04$. The decrease in $\chi_0$ with $x$ reflects the electron doping since band calculations show a negative $d\chi(E)/dE$ at Fermi level.$^{17,21}$ The extra susceptibility in the SC regime resembles the behavior of thermopower in SmFe$_{1-x}$CoAsO system,$^{23}$ implying the importance of spin fluctuations for the superconductivity. Besides, the enhanced spin fluctuations are also evidenced by the relatively high value of Wilson ratio, defined as $R_W = \frac{\pi^2 k_B^2}{3 J N J_N}$, where $\chi_{\text{core}}$ of LaFe$_{1-x}$Ni$_x$AsO is about $-1.0 \times 10^{-4}$ emu mol$^{-1}$. $\chi_0$ is thus about $3.7 \times 10^{-4}$ emu mol$^{-1}$ for $x = 0.04$, giving $R_W$ of 4.7.

It is noted that the maximum $T_c$ (6.5 K) in LaFe$_{1-x}$Ni$_x$AsO is merely one fourth of that in LaFeAsO$_{1-x}$F$_x$ and half of that in LaFe$_{1-x}$CoAsO.$^{23}$ The lowered $T_c$ in the Co-doped system was discussed in terms of the relatively small As-Fe-As angle,$^{23}$ according to an empirical structural rule for $T_c$ variations.$^{38}$ However, the As-Fe-As angle of LaFe$_{0.96}$Ni$_{0.04}$AsO is almost the same as that of LaFe$_{0.95}$Co$_{0.05}$AsO. Therefore, the much lowered $T_c$ in LaFe$_{1-x}$Ni$_x$AsO system should be caused by the reason other than structural aspect.

Let us turn to examine the normal-state property to find the possible clues. The normal-state resistivity strikingly exhibits a semiconducting-like behavior above $T_c$, as shown in Fig. 2. At first glance, the resistivity upturn at low temperatures might be ascribed to Anderson localization owing to the Ni incorporation, which might account for the lowered $T_c$. This scenario of disorder-induced localization would lead to a more profound resistivity upturn or higher $T^*$ (resistivity minimum temperature) with the increase in Ni doping. However, the $\rho(T)$ curves in Fig. 2 show that $T^*$ decreases monotonically with increasing $x$. Therefore, the evolution of the resistivity upturn with Ni doping suggests that Anderson localization is unlikely to be the main reason for the lowered $T_c$.

In the framework of a coherent-incoherent scenario,$^{39}$ the itinerant carriers and the local magnetic moments coexist in the undoped iron arsenides. Based on the logarithmic upturn of resistivity, a spin-flip scattering between the itinerant charge carriers and the local moments in the undoped FeAs layers has very recently been proposed.$^{40}$ It is noted that the spin-flip scattering (actually analog to Kondo effect) is already there in the parent compound. Upon electron doping, $T^*$ is suppressed due to the decrease in $N(E_F)$, as the Kondo energy scale $T_K \approx \sqrt{\gamma J N(E_F) \exp(-1/2 J N(E_F))}$ with $J$ being the Kondo coupling constant. In the case of Ni doping, both extra itinerant 3$d$ electrons and stabilized local moments (as inferred from the band structure calculation$^{21}$) are introduced. For the same electron doping level, one would expect an enhanced spin-flip scattering in the Ni-doped system. The spin-flip scattering competes with the SC Cooper pairing, which explains the suppression of $T_c$. Therefore, the narrow SC region as well as the much lowered $T_c$ in LaFe$_{1-x}$Ni$_x$AsO system is here ascribed to be a combined effect from the competing Kondo-like interactions, Anderson localization, as well as the structural variation.

Very recently, the effectiveness of Ni doping for SC has been also demonstrated in BaFe$_2$As$_2$ (Ref. 41) and CaFeAsF (Ref. 42) systems. The $T_{c,\text{max}}$ are 20.5 and 12 K, respectively. The variations in $T_c$ are possibly due to the Kondo-like interactions (not significant in Ni-doped BaFe$_2$As$_2$) as well as the structural difference. The bond angle of As-Fe-As in CaFeAsF is significantly smaller than that of LaFeAsO.

Figure 7 summarizes a SC phase diagram for LaFe$_{1-x}$Ni$_x$AsO system. With Ni-doping, the SDW order is suppressed, followed by the emergence of superconductivity. The SC region is particularly narrow and the $T_c$ is remarkably low, as compared with those of LaFeAsO$_{1-x}$F$_x$ and

| Samples | $\chi_0\times10^4$ | $\alpha\times10^3$ | $C$ |
|---------|------------------|------------------|-----|
| $x = 0$ | 3.27             | 3.6              | 0.0045 |
| $x = 0.01$ | 2.85             | 3.0              | 0.0070 |
| $x = 0.02$ | 2.45             | 4.1              | 0.0056 |
| $x = 0.03$ | 2.36             | 4.3              | 0.0038 |
| $x = 0.04$ | 2.71             | 3.4              | 0.0021 |
| $x = 0.05$ | 2.22             | 3.6              | 0.0027 |
| $x = 0.06$ | 2.00             | 3.8              | 0.0035 |
| $x = 0.10$ | 1.44             | 3.5              | 0.0098 |
LaFe$_{1-x}$Co$_x$AsO (see Table III). The normal state is divided by the line of $T^*$ into metallic and semiconducting regions. The “optimal” doping occurs at $x_{opt}=0.04$, which is about half of the $x_{opt}$ of LaFe$_{1-x}$Co$_x$AsO. This observation further demonstrates the itinerant character of Ni 3d electrons. Here we emphasize that the occurrence of superconductivity by Ni doping contrasts sharply with the cuprate superconductors, where the substitution of Cu with Ni in CuO$_2$ planes severely destroys the superconductivity.$^{13}$

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