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Strong-coupling superconductivity in the nickel-based oxypnictide $LaNiAsO_{1-x}F_x$

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A series of layered nickel-based $LaNiAsO_{1-x}F_x$ compounds with $x=0-0.15$ are synthesized by solid-state reactions. The pure LaNiAsO exhibits bulk superconductivity with $T_c \sim 2.75$ K. Partial substitution of oxygen with fluorine increases the transition temperature to ~3.8 K. The $LaNiAsO_{0.9}F_{0.1}$ sample shows a sharp superconducting transition and a sharp specific-heat jump at the critical temperature. The magnitude of the specific-heat jump is much larger than that expected from the weak-coupling BCS theory, indicating that this superconductor is in the strong-coupling regime. Furthermore, the temperature dependence of the specific heat deviates strongly from the theoretical result for the single-band *s*- or *d*-wave superconductor but shows a characteristic feature of multigap.

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Layered transition-metal oxypnictides La*M*PnO (*M*=Mn, Fe, Co, and Ni; Pn=P and As) have attracted great attention recently due to the discovery of superconductivity in Fe- and Ni-based systems. The superconductivity was first reported in Fe-based LaFePO with a transition temperature $T_c \sim 4$ K, which increases to 7 K with F^- doping,[1] and later in Ni-based LaNiPO with $T_c \sim 3$ K.[2] With the replacement of P with As and the partial substitution of O with F in the Fe-based compound $LaFeAsO_{1-x}F_x$, T_c rises to 26 K.[3] At present much effort has been devoted to the Fe-based systems.[4–10] It is found that the undoped compound LaFeAsO itself is not superconducting but undergoes a spin-density-wave (SDW) transition at 150 K. Upon fluorine doping, the SDW instability is suppressed, and the superconductivity starts to appear.[11] It is of great interest to see if a similar phenomenon could appear in the Ni-based superconducting compound LaNiPO when P is replaced with As and O is partially substituted with F.

In this work, we present an extensive investigation on the physical properties of high quality $LaNiAsO_{1-x}F_x$ ($x=0\sim0.15$) superconductors. We found that, unlike LaFeAsO, the pure LaNiAsO exhibits bulk superconductivity with $T_c \sim 2.75$ K. Partial substitution of oxygen with fluorine increases the transition temperature only slightly; however it dramatically improves the superconducting quality. The superconducting transition temperature becomes extremely narrow and the superconducting volume is very high. The transition width is about 0.05 K when the F content is higher than 0.06. The high quality of the sample enables us to determine accurately the superconducting parameters. Sharp specific-heat jumps at the superconducting transition temperatures were observed. Detailed analysis of the specific-heat data suggests that $LaNiAsO_{1-x}F_x$ is a strong-coupling and multigap superconductor.

The samples were synthesized by the solid-state reaction using NiO, Ni, As, La, and LaF_3 as starting materials. LaAs was prepared by reacting La chips and As pieces at 500 °C for 15 h and then at 850 °C for 2 h. The raw materials were thoroughly grounded and pressed into pellets. The pellets were wrapped into Ta foil and sealed in an evacuated quartz tube under argon atmosphere. It was then annealed at 1150 °C for 50 h. The resulting samples were characterized by powder x-ray diffraction (XRD) with Cu Kα radiation at room temperature. Figure 1 shows the XRD patterns for LaNiAsO and $LaNiAsO_{0.9}F_{0.1}$. These patterns can be well indexed on the basis of tetragonal ZrCuSiAs-type structure with the space group *P*4/*nmm*. Two tiny impurity peaks were detected for LaNiAsO but no obvious impurity phase was detected for $LaNiAsO_{0.9}F_{0.1}$. The lattice parameters are $a=0.4119$ nm and $c=0.8180$ nm for LaNiAsO and $a=0.4115$ nm and $c=0.8169$ nm for $LaNiAsO_{0.9}F_{0.1}$.

The electrical resistivity was measured by the standard four-probe method. The ac magnetic susceptibility was measured with a modulation field of 10 Oe at 333 Hz. The Hall-coefficient measurement was done using a five-probe technique. The specific heat was measured using a thermal relaxation calorimeter. The field dependence of the thermometer and the heat capacity of the addenda were carefully calibrated before measurement. All these measurements were

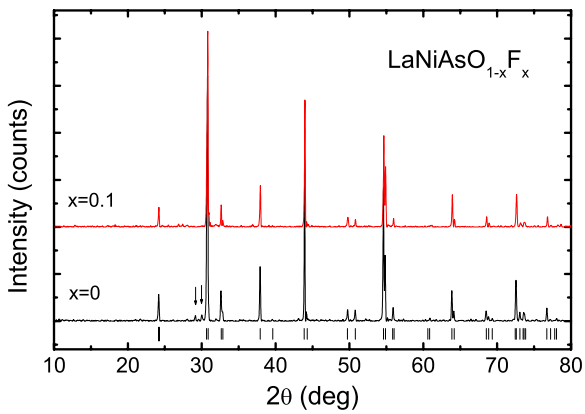

FIG. 1. (Color online) The x-ray-powder-diffraction patterns of LaNiAsO and $LaNiAsO_{0.9}F_{0.1}$. The bars at the bottom show the calculated Bragg-diffraction positions of LaNiAsO. Two tiny peaks marked by arrows are from the impurity phase of LaNiAsO. No impurity phase is detected for $LaNiAsO_{0.9}F_{0.1}$.

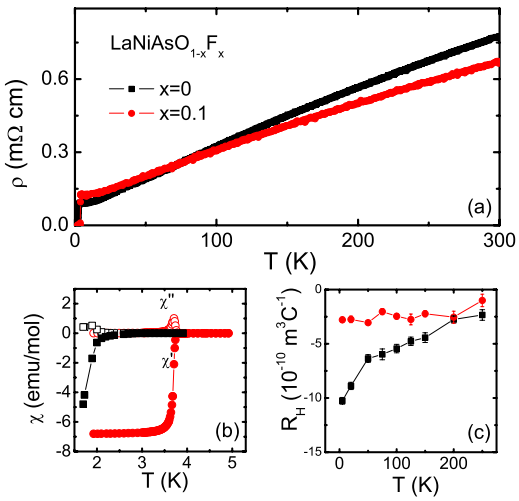

FIG. 2. (Color online) (a) Temperature dependence of the resistivity ρ for LaNiAsO and $LaNiAsO_{0.9}F_{0.1}$. (b) The real and the imaginary parts of ac susceptibility below 5 K for LaONiAs (open and closed squares) and $LaNiAsO_{0.9}F_{0.1}$ (open and closed circles), respectively. (c) Hall coefficient versus temperature for the two samples.

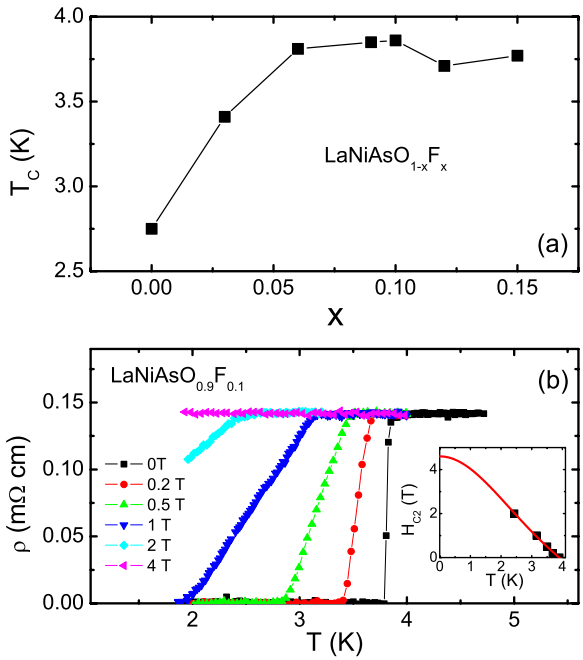

FIG. 3. (Color online) (a) Doping dependence of the superconducting transition temperature T_c for $LaNiAsO_{1-x}F_x$. (b) Temperature dependence of the resistivity of $LaNiAsO_{0.9}F_{0.1}$ at different fields. The inset shows the temperature dependence of the upper critical magnetic field.

preformed in a physical property measurement system (PPMS) of the Quantum Design company.

Figure 2(a) shows the temperature dependence of the resistivity ρ for LaNiAsO and $LaNiAsO_{0.9}F_{0.1}$ from 1.8 to 300 K at zero field. The resistivity of LaNiAsO is metallic, different from that observed in LaFeAsO. In LaFeAsO, the resistivity exhibits a SDW transition at ~150 K, a minimum at ~100 K, and an upturn at low temperatures.[3,11] The onset superconducting transition occurs at 2.75 K for LaNiAsO and at 3.8 K for $LaNiAsO_{0.9}F_{0.1}$. The transition temperature of LaNiAsO is close to that of LaNiPO, with $T_c \sim 3$ K, but differs from that of LaFeAsO, which is nonsuperconducting and with a structural and SDW transition below 150 K. The superconducting transition width for $LaNiAsO_{0.9}F_{0.1}$ is ~0.05 K, much narrower than that for any other superconductor in this family, indicating the high homogeneity of the superconducting phase.

The bulk superconductivity in these samples was confirmed by magnetic-susceptibility measurements. Figure 2(b) shows the real (χ') and imaginary (χ'') ac susceptibilities around T_c. Both LaNiAsO and $LaNiAsO_{0.9}F_{0.1}$ samples become diamagnetic below T_c. The transition of $LaNiAsO_{0.9}F_{0.1}$ is much steeper than that of LaNiAsO. For pure LaNiAsO, χ' begins to drop below 1.8 K, similar to that for LaNiPO.[2] However, for $LaNiAsO_{0.9}F_{0.1}$, χ' is already saturated below 3 K. The absolute value of the diamagnetic susceptibility is about three times larger than that reported for $LaFeAsO_{1-x}F_x$, LaFePO, and LaNiPO samples. The typical diamagnetic-susceptibility values of these superconductors are about 2 emu/mol at low temperatures. This indicates that the volume fraction of superconducting phase in this sample is very high.

The temperature dependence of the Hall coefficient R_H for $LaNiAsO_{1-x}F_x$ with $x=0$ and 0.1 is shown in Fig. 2(c). The negative R_H implies that the charge carriers are dominantly electron type, same as in $LaFeAsO_{1-x}F_x$.[9] The absolute value of R_H for $LaNiAsO_{0.9}F_{0.1}$ is more than 1 order of magnitude smaller than that of $LaFeAsO_{0.9}F_{0.1}$, possibly indicating that the $LaNiAsO_{1-x}F_x$ system has a relatively higher carrier density if we adopt simply the one-band formula $R_H = 1/ne$. Assuming that the electron and hole mobilities have the same temperature dependence, the higher carrier density in $LaNiAsO_{1-x}F_x$ can be explained by the fact that $Ni^{2+}(3d^8)$ contributes two more electrons than $LaFeAsO_{0.9}F_{0.1}$ does. The Fermi energy shifts up. Compared with that of $Fe^{2+}(3d^6)$ in $LaOFeAs_{1-x}F_x$, the hole bands tend to be fully filled. As a result predicted by band calculations,[6] the electron bands dominate the conductivity in LaNiAsO.

Figure 3(a) shows T_c as a function of x for $LaNiAsO_{1-x}F_x$. With increasing x, T_c first increases from 2.75 for $x=0$ to 3.78 K for $x=0.06$ and then remains almost constant up to $x=0.15$. This doping dependence of $T_c(x)$ is similar to that of the $LaFeAsO_{1-x}F_x$ system.[3] The superconducting transition width is about 0.05 K when x is higher than 0.06.

Figure 3(b) shows the field dependence of the resistivity of $LaNiAsO_{0.9}F_{0.1}$ up to 4 T. The transition temperature T_c shifts to lower temperature in external magnetic fields. The transition width is gradually broadened, similar to that for LaFeAsO.[9] Since LaNiAsO and related materials are layered compounds with strong anisotropy,[1,2] the field-induced broadening may result from the anisotropy of the upper critical field H_{c2} for $H \| c$ and $H \| ab$ plane. Such a broadening effect was also observed in layered $Li_{0.68}NbO_2$ and high T_c cuprates.[12,13] A 4 T magnetic field suppresses T_c down below 1.8 K. Using the onset superconducting transition temperature, the zero temperature upper critical field $H_{c2}(0)$ can be estimated by using the formula $H_{c2}(T) = H_{c2}(0)(1-t^2)/(1$

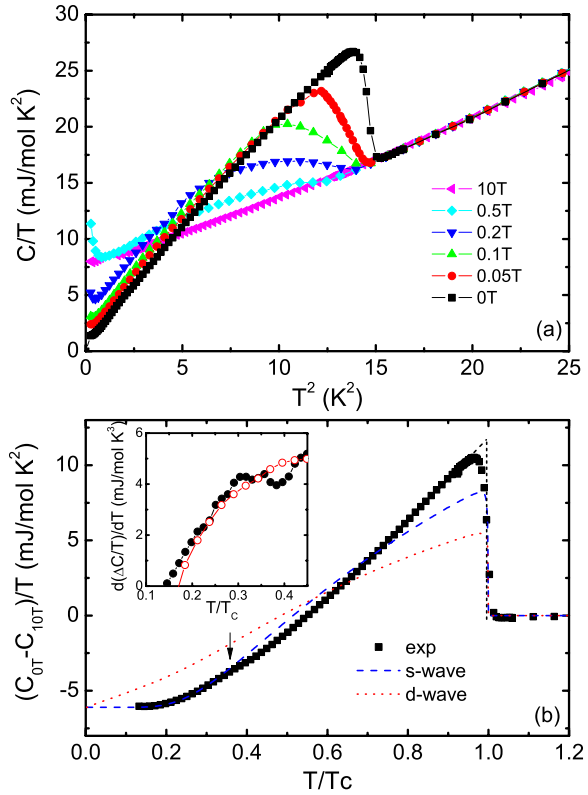

FIG. 4. (Color online) (a) C/T versus T^2 of $LaNiAsO_{0.9}F_{0.1}$ under selected magnetic fields. (b) Temperature dependence of the difference between the specific-heat coefficients at zero field and at 10 T, $(C_{0\ T}-C_{10\ T})/T$. The dashed and dotted lines are theoretical curves for the BCS s- and d-wave superconductors, respectively. Inset: Temperature dependence of $d(\Delta C/T)/dT$ at zero field (closed circles) and $H=0.2$ T (open circles).

$+t^2$),[9,10] where t is the reduced temperature, $t=T/T_c$. By fitting, we find that $H_{c2}(0)\sim 4.6$ T [see inset of Fig. 3(b)], which is about ten times smaller than the corresponding value for 10% F-doped LaFeAsO ($H_{c2}\sim 54$ T).[9] The relatively lower H_{c2} in $LaNiAsO_{0.9}F_{0.1}$ is probably due to the lower T_c in this material.

Specific-heat (C) measurement is a powerful tool for detecting the bulk properties of a superconductor both in the superconducting and normal states. Generally, the specific heat is dominated by the phonon contribution and it is difficult to separate the electronic contribution from the total specific heat at high temperatures. Therefore, there is a large uncertainty in the determination of the characteristic parameters, such as the normal-state electronic specific-heat coefficient γ_n and the specific-heat jump at T_c, if the measurement of the specific heat is done for a superconductor with a higher T_c. For example, in $LaFeAsO_{0.9}F_{0.1}$, with $T_c\sim 20$ K, the specific-heat anomaly at T_c has not been observed at zero field.[10] However, the high superconducting volume fraction and the low transition temperature in our $LaNiAsO_{0.9}F_{0.1}$ sample provide a good opportunity to determine these superconducting parameters accurately.

Figure 4(a) shows the specific-heat coefficient C/T as a function of T^2 from 0.5 to 5 K for $LaNiAsO_{0.9}F_{0.1}$ in a set of external fields. At zero field, the bulk nature of superconductivity and the high quality of the sample are confirmed by the steep jump in C/T at $T_c=3.8$ K, consistent with the resistivity measurement. A small field of 0.05 T suppresses substantially the specific-heat jump at T_c. A small upturn in C/T at low temperature is observed at 0.5 T, which can be attributed to the Schottky anomaly resulting from the contribution of a small amount of magnetic impurities. A similar low-temperature upturn in the specific heat due to Schottky anomaly was observed for $YBa_2Cu_3O_7$.[14]

Above T_c, C/T shows a good linear T^2 dependence. By fitting the normal-state specific heat C with the formula $C=\gamma_n T+\beta T^3$, it is found that $\gamma_n=4.75$ mJ/mol K^2 and $\beta=0.808$ mJ/mol K^4. If these parameters are used to extract the phonon contributions below T_c, it is found that the entropy difference between the superconducting and normal states is not conserved above T_c. This suggests that the above formula of the specific heat, i.e., $C=\gamma_n T+\beta T^3$, might be too simple to account for the experimental data below T_c and the value of γ_n obtained above is not correct.

To resolve the above problem, we apply a 10 T magnetic field to suppress completely the superconductivity and the low-temperature Schottky anomaly. Thus the specific heat at 10 T contains only the contribution from normal-state electrons and phonons. By subtracting these normal-state contributions at 10 T from the zero-field specific heat [Fig. 4(b)], the normal-state electronic specific-heat coefficient is now found to be $\gamma_n=7.3$ mJ/mol K^2. This value of γ_n is larger than that estimated from the normal-state data by simply subtracting a T^3 phonon contribution. It is smaller than the corresponding value for other layered superconductors, such as $NaCoO_2$ (~ 24 mJ/mol K^2),[15,16] Sr_2RuO_4 (~ 40 mJ/mol K^2),[17] and Li_xNbS_2 (~ 10 mJ/mol K^2),[18] but larger than that of Li_xNbO_2 (~ 3.59 mJ/mol K^2).[12] In the absence of magnetic field, the low-temperature C/T extrapolates to a small but finite value of $\gamma_s=1.16$ mJ/mol K^2. This residual specific heat indicates that there is a residual density of states at the Fermi level. From this residual specific heat, the superconducting volume fraction of the sample is estimated to be about $(\gamma_n-\gamma_s)/\gamma_n=84\%$. This value of superconducting volume fraction is rather high compared with those of other previously reported Fe- or Ni-based superconductors, with a typical superconducting volume fraction of less than 50%.[1–3,9]

Figure 4(b) shows the difference between the specific-heat coefficients at 0 and 10 T, $(C_{0\ T}-C_{10\ T})/T$, as a function of T/T_c. The entropy is now conserved above T_c. The normalized specific-heat jump at T_c of $LaNiAsO_{0.9}F_{0.1}$ is found to be $\Delta C/(\gamma_n-\gamma_s)T_c=1.9$, which is significantly larger than the value predicted by the weak-coupling BCS theory. This large specific-heat jump may result from strong electron-phonon coupling. If the electron-phonon mechanism of superconductivity is assumed, one can then estimate the electron-phonon coupling constant λ from the modified McMillian formula,[19–21]

$$\lambda=\frac{1.04+\mu^*\ln(\omega_{\ln}/1.2T_c)}{(1-0.62\mu^*)\ln(\omega_{\ln}/1.2T_c)-1.04}, \qquad (1)$$

where μ^* is a Coulomb pseudopotential and $\omega_{\ln}$ is a logarithmic averaged phonon frequency. $\omega_{\ln}$ can be

determined from the specific-heat jump at T_c using the formula $\Delta C/\gamma_n T_c = 1.43[1+53(T_c/\omega_{\ln})^2 \ln(\omega_{\ln}/3T_c)]$. Taking $\mu^* = 0.10$ and $T_c = 3.8$ K, we obtained $\omega_{\ln} = 61.6$ K and $\lambda = 0.93$. The large value of λ confirms the strong-coupling nature of the superconducting pairing.

The value of λ can be also estimated from the effective-mass normalization. From the first-principles calculations, it was found that the bare electronic specific-heat coefficient for LaNiAsO is $\gamma_0 = 3.81$ mJ/mol K^2.[6] By substituting this value into the formula $\gamma_n = (1+\lambda)\gamma_0$, we find that $\lambda = 0.92$ if $LaNiAsO_{0.9}F_{0.1}$ have the same value of γ_0 as LaNiAsO. This value of λ agrees well with that estimated from the specific-heat jump at T_c.

The specific-heat data below T_c can be used to determine the pairing symmetry.[12] Figure 4(b) compares the experimental data of $LaNiAsO_{0.9}F_{0.1}$ with the BCS mean-field results for a single-band *s*- or *d*-wave superconductors. Apparently the theoretical curves for both the single-band *s*- and *d*-wave superconductors deviate significantly from the experimental data. Moreover, a tiny board hump is observed at $T \sim 1.35$ K [indicated by an arrow in Fig. 4(b)]. The inset of Fig. 4(b) shows the temperature dependence of $d(\Delta C/T)/dT$, where $\Delta C = C(H) - C(10\ \mathrm{T})$. We can see more clearly the hump feature in the $d(\Delta C/T)/dT - T$ curve in zero field. However, this hump is suppressed by a magnetic field of 0.2 T. This is a typical feature of a multiband system, since the superconducting gap may vary at different bands and the smaller gap can have a greater contribution to the low-temperature specific heat. A similar behavior was observed in MgB_2, where the low-temperature specific heat shows a broad peak at about $1/4T_c$ in addition to a sharp specific-heat jump at T_c.[22]

In summary, high quality $LaNiAsO_{1-x}F_x$ superconducting samples with extreme narrow superconducting transition width of ~ 0.05 K and high superconducting volume fraction are synthesized. The upper critical field is found to be 4.6 T for $LaNiAsO_{0.9}F_{0.1}$. A sharp specific-heat jump (ΔC) is observed at the transition temperature, $\Delta C/\gamma_n T_c = 1.9$, which is much larger than the value predicted by the weak-coupling BCS theory. This large specific-heat jump indicates that the superconducting pairing is in the strong-coupling regime if the electron-phonon mechanism is assumed. The presence of a hump at about 1.35 K in specific heat and the deviation of the specific-heat data from the BCS result for the single-band *s*- or *d*-wave superconductor suggest that this material is a multisuperconducting gap system.

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