Multiple Phase Transitions in Single-Crystalline Na$_{1-\delta}$FeAs

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The recent discovery of superconductivity with transition temperature $T_c \sim 26$ K in LaFeAsO$_{1-x}$F$_x$ (abbreviated as 1111) has attracted a great deal of research interest [1]. Substituting La with other rare earth elements dramatically enhances the $T_c$ up to 41–55 K [2–5]. At room temperature, all these parent compounds crystallize in a tetragonal ZrCuSiAs-type structure, which consists of alternate stacking of edge-sharing Fe$_2$As$_2$ tetrahedral layers and La$_2$O$_2$ tetrahedral layers along the $c$ axis. Soon after this discovery, another group of compounds AFe$_2$As$_2$ ($A = Ba, Sr, Ca$)(122), which crystallize in a tetragonal ThCr$_2$Si$_2$-type structure with identical Fe$_2$As$_2$ tetrahedral layers as in LaFeAsO, were also found to be superconducting with $T_c$ up to 38 K upon hole doping [6–8].

In these so called “1111” and “122” compounds, it is well known that the Fe ions tend to form magnetically ordered states and participate in building up a high density of states at the Fermi level, which is responsible for the “1111” magnetic ground state, similar to the parent compounds of 1111 [10,11]. The absence of superconductivity was indeed found in the nearly stoichiometric LiFeAs synthesized by high pressure method. However, there is little experimental evidence for structural or magnetic transition. It may be due to Li deficiency, which introduces the level of carrier density close to a “critical value” just suppressing the spin-density-wave (SDW) order.

It is of great interest to investigate the electronic properties of the high-quality single crystal of these materials (111) and compare them with 1111 and 122 systems. Here we report on a comprehensive study of the transport, specific heat, and magnetic susceptibility on nearly stoichiometric single crystals of Na$_{1-\delta}$FeAs. We find that Na$_{1-\delta}$FeAs single crystal undergoes three successive phase transitions at 52, 41, and 23 K, which might correspond to structural, magnetic and superconducting transitions, respectively. Hall coefficient measurement indicates the development of energy gap at low temperature in Na$_{1-\delta}$FeAs, which is similar to LaFeAsO and SrFe$_2$As$_2$. This is consistent with the expectation of recent density functional calculation which shows the SDW instability for stoichiometric NaFeAs [14]. The present work provides a strong evidence that a stoichiometric NaFeAs has a magnetic ground state, similar to the parent compounds of 1111 and 122.

High-quality single crystals of Na$_{1-\delta}$FeAs have been grown by the self-flux technique. The starting compositions were selected as Na$_{1-\delta}$FeAs. The mixtures of Na, and FeAs were put into an alumina crucible and sealed in Ta crucible under 2 atm of argon gas. The Ta crucible was then sealed in an evacuated quartz ampoule and heated to 1100°C and cooled slowly (at 5°C/h) to grow single crystals. The obtained crystals with sizes up to 8 mm × 5 mm × 0.5 mm have the form of platelets with shiny surfaces. These crystals were characterized by X-ray diffraction (XRD). Figure 1 shows the x-ray diffraction pattern of Na$_{1-\delta}$FeAs with the 00$l$ reflections. The lattice constant $c = 7.028$ Å was calculated from the higher order peaks, comparable to that of polycrystalline sample [13].
The elemental composition of the single crystal was checked by Inductively Coupled Plasma (ICP) analysis. Several crystals from the same batch were analyzed and the deficiency of sodium was found to be less than 1%; that is, the elemental composition of the single crystal is very close to a stoichiometric 1:1:1. The resistivity was measured by a standard 4-probe method. The dc magnetic susceptibility was measured with a magnetic field of 0.1 T. The Hall coefficient measurement was done using a five-probe technique. The specific heat measurement was carried out using a thermal relaxation calorimeter. These measurements were performed down to 2 K in a physical property measurement system (PPMS) of Quantum Design.

Figure 2(a) shows the temperature dependence of in-plane resistivity \( \rho_{ab} \) of \( \text{Na}_1\text{FeAs} \) at zero field. At high temperature, \( \rho_{ab} \) shows a metallic behavior, whereas \( \rho_{ab} \) increases steeply below 52 K with a shoulder around 41 K, and then shows a superconducting transition near 23 K (drops to zero resistivity at 8 K). The superconducting transition seems to be broad, similar to that of polycrystalline \( \text{LaFeAsO} \) where the superconducting transition is broadened strongly in magnetic fields due to the weak link between superconducting grains [18]. Figure 2(d) shows \( H_{c2}(T) \) for both \( H \parallel ab \) and \( H \parallel c \), respectively, where \( T_c \) is defined by a criterion of 50% of normal state resistivity. The curves \( H_{c2}(T) \) are very steep with slopes \( -dH_{c2}/dT \sim 3.98 \text{T/K for } H \parallel ab \) and \( -dH_{c2}/dT \sim 2.19 \text{T/K for } H \parallel c \). Using the Werthamer-Helfand-Hohenberg formula [19], \( H_{c2}(0) \), and taking \( T_c = 15 \text{ K} \), the upper critical fields are estimated as \( H_{c2} = 41.2 \text{T} \) and \( H_{c2} = 22.7 \text{T} \), respectively. Regarding the relatively low value of \( T_c \), the upper critical fields \( H_{c2}(0) \) seem to be very high. The anisotropy ratio \( \gamma = H_{c2}^{ab}/H_{c2}^{c} = 1.8 \) is rather small, which is close to that of \( \text{Sr}_2\text{Fe}_2\text{As}_2 \) with \( \gamma = 2.0 \) [17]. It is much lower than high \( T_c \) cuprates, for example \( \gamma = 7-10 \) for \( \text{YBCO} \) [20]. The lower value of \( \gamma \) indicates that the interplane coupling in \( \text{Na}_1\text{FeAs} \) is relative strong and the energy band with strong dispersion along the \( z \) direction may play an important role in understanding the superconductivity of \( \text{Fe-based superconductors} \).
In Fig. 3(a), we present the temperature dependence of magnetic susceptibility $\chi$ for Na$_{1-x}$FeAs in a field of 0.1 T with the $H \parallel ab$ plane and $H \parallel c$ axis, respectively. At high-temperature, $\chi$ decreases monotonically with decreasing temperature. This non-Pauli and non-Curie-Weiss-like paramagnetic behavior, is consistent with those observed in 1111 and 122 parent compounds above $T_{\text{SDW}}$ [1,17,21]. At low temperature, $\chi$ tends to show a small upturn, and followed by a clear diamagnetic drop corresponding to superconductivity at around 10 K, which corresponds to the zero resistivity temperature. To show the low temperature part clearly, we have plotted in the inset of Fig. 3(a) the susceptibility in the temperature interval from 30 to 60 K. Two humps found in $\chi$ with magnetic field $H$ parallel to the $ab$ plane at 40 and 50 K give that the magnetic easy axis of this compound is along the $ab$ plane (There is no detectable anomaly observed in $\chi$ with $H \parallel c$). That is to say, the Fe spins in NaFeAs order antiferromagnetically with spin direction parallel to the $ab$ plane, similar to that of SrFe$_2$As$_2$, which has been confirmed by neutron scattering experiment [22].

To get more information about the structural or magnetic phase transition, we performed specific heat measurements for Na$_{1-x}$FeAs. Figure 3(b) shows the temperature dependence of $C/T$ from 2 to 60 K. Two successive jumps in $C/T$ at $T_1 \sim 41$ K and $T_2 \sim 52$ K show the bulk nature of phase transitions which have been observed in susceptibility and resistivity data as well. However, the anomalies around $T_1$ and $T_2$ are very broad and small, which would be characteristic of a second-order transition. Very similar properties have been reported on 1111 compounds, such as LaFeAsO, where two subsequent jumps at 155 and 143 K were observed in specific heat data corresponding to the structural and SDW transitions, respectively [23]. While the structural transition and SDW transition occur at same temperature in SrFe$_2$As$_2$. The specific heat shows a very sharp peak which is the characteristic feature of first-order phase transitions [17]. The conversion of first-order transition to second-order transition has also been observed in those of slightly underdoped samples of BaFe$_{2-x}$Co$_x$As$_2$ ($x < 0.2$), in which the single structural or magnetic phase transition splits into two distinct phase transitions (The first-order phase transition starts rounding off and becomes smaller as more Co ions are added in the pure system) [24].

The onset of a second-order phase transition is probably related to a change of symmetry in the ground state [25,26]. Theoretical studies also suggest that whether the structural and magnetic transitions occur simultaneously or separately depends on the interlayer coupling [25,26]. The separation of structural distortion and the magnetic transition in the present compound indicates that the interlayer coupling is closer to that of 1111 compounds, but much weaker than 122 compounds.

At low temperature, there is no detectable anomaly observed around $T_c$, indicating a small superconducting volume fraction; the fit of $C/T$ vs $T^2$ yields the electronic coefficient $\gamma \approx 5$ mJ/mol $\cdot$ K$^2$, as shown in the upper inset of Fig. 3(b). Here the electronic coefficient for Na$_{1-x}$FeAs is close to the values for LaFeAsO and SrFe$_2$As$_2$ (which are significantly smaller than the theoretical calculations due to the SDW partial gap) [9,17].

The Hall coefficient $R_{H}$ as a function of temperature between 20 and 200 K for Na$_{1-x}$FeAs is shown in Fig. 4. The Hall coefficient is negative at all temperatures, indicating conduction carriers are dominated by electrons. Above 50 K, the Hall coefficient is nearly temperature independent; the carrier density is estimated being $n = 9 \times 10^{21}$ cm$^{-3}$ at 200 K if the one-band model is simply adopted. It is comparable to that of SrFe$_2$As$_2$ with $n = 1.5 \times 10^{22}$ cm$^{-3}$ at 300 K obtained by the same method. The large carrier number for Na$_{1-x}$FeAs indicates that it is a good metal. Noted that the band calculation on its sister compound of LiFeAs revealed its semimetallic behavior. As mentioned above, there is a possibility that Na defi-
ciencies serve as a source of effective hole carriers. So it is an extremely rare case the measurement of a negative Hall coefficient in nominally hole-doped Fe-based superconductors. However, this behavior could be qualitatively understood by a simple two-band approximation. In a scenario where the Fermi surface contains both electron and hole pockets, the sign of $R_H$ depends on the relative magnitude of the respective densities, $n_e$ and $n_h$, and mobilities, $\mu_e$ and $\mu_h$ ($\mu = e\tau/m^*$, where $e$ is the electron charge, $1/\tau$ is the scattering rate and $m^*$ the effective mass). And therefore, in the "hole"-doped sample, the negative $R_H$ implies that $\mu_e$ is much larger than $\mu_h$.

Below 50 K, $R_H$ drops dramatically to a very large negative value. The absolute value of $R_H$ at 23 K is about 60 times larger than that at 60 K. The huge increase of the $R_H$ value is seen in the undoped compounds of 1111 and 122, which is naturally explained by the thinning of the Fermi surface which removes a large part of free carriers. Evidence for the gap is also observed by optical spectroscopy measurement [27]. The band calculation shows that a hole pocket is also observed by optical spectroscopy measurements [27]. The band calculation shows that a hole pocket is also observed by optical spectroscopy measurement [27]. The band calculation shows that a hole pocket is also observed by optical spectroscopy measurement [27].

In summary, we have succeeded in growing the high-quality single crystal of nearly stoichiometric Na$_{1-x}$FeAs and studied the electronic properties by measurements of electrical resistivity, heat capacity, and Hall effect. This compound is found to undergo a structural, magnetic and superconducting transitions at low temperatures. The negative Hall coefficient $R_H$ suggests that the electron type charge carriers dominate the conduction in this material. Although the present experiments cannot completely rule out a tiny amount of Na deficiencies, our present data provide the first direct experimental evidence confirming the existence of SDW instability in NaFeAs, which are consistent with the theoretical predication. We believe that our results are important to understand the mechanism of superconductivity and underline further the importance of magnetic fluctuations for the superconducting pairing observed in Fe-based superconductors.

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Note added.—In the published version of [13], new $\mu$SR data were added to the original preprint indicating the presence of magnetic order near 40 K, which thus supports the conclusion of present work about magnetic ordering.


