Phase diagram and weak-link behavior in Nd-doped CaFe$_2$As$_2$

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Abstract

The transport properties, phase diagram, and dopant distribution are investigated in systematically Nd-doped CaFe$_2$As$_2$ single crystals. Coexistence of two superconducting (SC) phases with different critical transition temperature ($T_c$) is observed. The low-$T_c$ phase emerges as $x \geq 0.031$, and the $T_c$ value increases to its maximum value of about 20 K at $x = 0.083$, the maximum doping level in our study. As $x \geq 0.060$, the high-$T_c$ phase with a $T_c$ value of about 40 K is observed. The structure transition (STr) from tetragonal to orthorhombic phase vanishes suddenly around $x = 0.060$, where a new STr from tetragonal to collapsed tetragonal phase begins to turn up. Compared to the low-$T_c$ phase, the end point of SC transition of the high-$T_c$ phase is more sensitive to the magnetic field, showing a characteristic of Josephson weak-link behavior. Possible scenarios about this system are discussed based on our observations. We also find that the non-uniform SC properties cannot be attributed to the heterogeneous Nd distribution on the micro scale, as revealed by the detailed energy dispersive x-ray spectroscopy measurements.

Keywords: Fe-based superconductors, Nd-doped CaFe$_2$As$_2$, phase diagram, weak-link behavior
1. Introduction

Fe-based superconductors have been studied extensively since the report of LaFeAsO$_{1-x}$F$_x$ with a $T_c$ of 26 K [1, 2]. Among the different systems, the AFe$_2$As$_2$ compounds (A = Ba, Sr, Ca and Eu, so called ‘122’ system) with the ThCr$_2$Si$_2$-type structure [3] are widely studied because single crystals with high quality are easily accessible [4]. The parent compounds of the 122 system undergo a phase transition from a high temperature tetragonal, paramagnetic phase (T phase) to a low temperature orthorhombic, antiferromagnetic phase (O phase). The antiferromagnetic order can be systematically suppressed and superconductivity can develop by the means of chemical substitution or applying pressure. The highest $T_c$ value in the 122 system is still lower than 55 K in the RFeAsO (1111; R = rare-Earth elements) system [5]. Superconductivity with a maximum $T_c$ of 38 K has been achieved in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ by hole-doping [6]. Meanwhile, electron-doping usually induces superconductivity at a lower temperature (around 22 K) by substituting Fe ions with other transition metals [7–9]. This is typically attributed to the imperfection of the FeAs conducting layers induced by doping.

In order to further enhance the $T_c$, much attention has been paid to electron doping approached by substitution of trivalent rare-Earth elements ions (Re$^{3+}$) on divalent A$^{2+}$ ions in the 122 system without affecting the FeAs layers [10–16]. However, superconductivity in single-crystalline samples is only attained in systems based on CaFe$_2$As$_2$. Besides the T–O transition at ambient pressure for CaFe$_2$As$_2$, the tetragonal phase transforms to a new collapsed tetragonal structure (cT, both the $a$-axis and $c$-axis lattices shrink) when a hydrostatic pressure (>0.35 GPa) is applied [17, 18]. Recently, it is found that this cT phase can be stabilized at ambient pressures by doping Pr or Nd into CaFe$_2$As$_2$. In contrast, the substitution of up to 28% La or 17% Ce does not drive this T–cT transition [12]. More surprisingly, two superconducting (SC) phases with $T_c$ of about 20 K and 40–49 K respectively were discovered in the rare-Earth-doped Ca$_{1-x}$Re$_x$Fe$_2$As$_2$ (Re = La, Ce, Pr and Nd) compounds, regardless of this T–cT structural evolution [12–16]. Although the high-$T_c$ phase exceeds the highest $T_c$ ~ 38 K in the hole-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$, the SC volume fraction is very low suggesting the absence of bulk superconductivity. The origin of the non-bulk and two-phase superconductivity has been attributed to the minor foreign phase, interface or filamentary superconductivity, Josephson junction coupling between grains et al, which is still an open issue and needs more in-depth investigations [14, 19, 20].

To the best of our knowledge, a systematic investigation on the Nd-doped CaFe$_2$As$_2$ system is still lacking. Moreover, the temperature versus doping phase diagram of this system is still not clear. In the present work, we report a systematic investigation on the characterization and phase diagram of electron-doped Ca$_{1-x}$Nd$_x$Fe$_2$As$_2$ single crystals. The behaviors of field induced resistance broadening for SC transition are also observed, indicating a weak-link feature in the present system.

2. Experimental details

Single crystals of systematically Nd-doped CaFe$_2$As$_2$ were grown using a self-flux method. The FeAs precursor was synthesized by the reaction of Fe powder and As chips at 700 °C for 20 h in a vacuum quartz tube. Appropriate amounts of the starting materials of FeAs, Ca and Nd with the ratio of 4:(1–x):x were placed in an alumina crucible, and sealed in an arc-welded iron tube.
The sample was heated to 1200 °C slowly and held for 5 h, and then cooled to 1030 °C with a rate of 3–6 °C h⁻¹ to grow the single crystals. The obtained single crystals show a shiny surface and are easily cleaved into plates.

The phase identification and crystal structure were characterized by x-ray diffraction (XRD) with Cu K radiation. The actual Nd concentrations were checked and determined by the energy dispersive x-ray spectroscopy (EDS) measurements. The resistance measurements with magnetic fields up to 9 T were carried out by using a standard four-contact method with a quantum design physical property measurement system (PPMS).

3. Results and discussion

Figure 1(a) shows the XRD θ–2θ patterns for four typical Ca₁₋ₓNdₓFe₂As₂ single crystals with different doping levels. The sharp (00l) diffraction peaks suggest that the crystallographic c-axis is perpendicular to the plane of the single crystals with an excellent crystalline quality. The calculated c-axis lattice parameters as a function of Nd content are plotted in figure 1(b). The data of the parent phase are taken from the report by S R Saha et al [12]. It can be found that the c-axis shrinks monotonously with increasing x, which implies a successful chemical substitution and is also consistent with previous reports [12].
Figure 2 presents the temperature dependence of resistivity under zero fields for Ca$_{1-x}$Nd$_x$Fe$_2$As$_2$ single crystals, normalized to the data at 300 K. The data of parent phase are taken from the report by another group [12]. Several features are observed at different temperatures. In the inset of figure 2, we denote them by arrows for the sample with $x=0.060$ as an example, where $T_O$, $T_{cT}$, $T_{cH}$, and $T_{cL}$ represent the transition temperature to the orthorhombic phase, to the collapsed tetragonal phase, the onset transition temperature of the high-$T_c$ phase, and that of the low-$T_c$ phase, respectively.

From our data we can see that with Nd doping the resistivity anomaly due to the tetragonal to orthorhombic structure transition (STr) shifts gradually to lower temperature and disappears around $x=0.060$. Another conspicuous feature is a sharp and dramatic drop in resistivity when the doping level $x \geq 0.060$. This feature is associated with a STr from the T phase to the cT phase [12, 17]. We note that there exists a hysteresis for the T–cT STr with increasing and decreasing temperature. Here we only show the data collected with increasing temperature. With increasing $x$, this resistivity transition shifts to higher temperatures, which is similar to that observed in Ca$_{1-x}$Pr$_x$Fe$_2$As$_2$ based on neutron-diffraction measurements [12]. For the sample with $x=0.060$, the coexistence of two structure transitions may be due to the local inhomogeneity. Along with the suppression of the T–O phase transition, resistivity decreases quickly below 10 K as $x \geq 0.031$, suggesting the appearance of a SC transition. When $x \geq 0.060$, two SC transition steps appear in the low temperature region, which seems to be a common feature in Ca$_{1-x}$Re$_x$Fe$_2$As$_2$. Both SC transitions are broad and no zero resistance was observed in some of the samples down to 2 K.

Based on the resistivity behaviors described above, we can establish a doping-temperature ($x$-$T$) phase diagram for Ca$_{1-x}$Nd$_x$Fe$_2$As$_2$, which is shown in figure 3. In the lower-doped side ($x \leq 0.060$), superconductivity of the low-$T_c$ phase coexists with the T–O transition. Similar behaviors have also been observed in the hole-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [21], electron-doped BaFe$_{2-x}$Co$_x$As$_2$ [22] and other rare-Earth-doped CaFe$_2$As$_2$ systems [13]. The suppression rate of the $T_O$ temperature in Ca$_{1-x}$Nd$_x$Fe$_2$As$_2$ is much larger than that of Ca$_{1-x}$La$_x$Fe$_2$As$_2$, in which the T–O transition is absent when the doping level of La $x>0.13$ [13]. When the doping level increases to 0.060, the T–O STr vanishes suddenly and a new T–cT STr begins to turn up. At
the same time, the high-$T_c$ phase emerges with an almost invariable $T_c$ value of about 40 K. In contrast, the $T_c$ value of the low-$T_c$ phase is monotonically increased from 10 K to about 20 K with $x$ increasing. Unlike other rare-Earth-doped CaFe$_2$As$_2$, both SC phases are detected clearly from the resistivity data in the high-doped range in our system, meaning that at least the high-$T_c$ phase doesn’t form a continuous percolative path for the current. This may be due to the lower solubility limit of the Ca$_{1-x}$Nd$_x$Fe$_2$As$_2$ compounds. In the Ca$_{1-x}$La$_x$Fe$_2$As$_2$ system, only the high-$T_c$ phase can be detected by transport measurements, when the doping level $x \geq 0.21$ [13]. Nevertheless, the distinct coexistence of two SC transitions in resistivity facilitates our investigation on the intrinsic natures of the two SC phases (see the next paragraph). Comparing our results with other reports on La- and Pr-doped CaFe$_2$As$_2$ systems, it is concluded that the high-$T_c$ phase appears at the doping level when the structural (T–O)/antiferromagnetic phase transition is totally suppressed. This is further demonstrated recently by the high pressure work on Ca$_{1-x}$La$_x$Fe$_2$As$_2$ samples [23]. One distinct feature for our phase diagram is the presence of the cT structure in the high doping region $0.060 \leq x \leq 0.083$, which is absent in the Ca$_{1-x}$La$_x$Fe$_2$As$_2$ system [13]. This may suggest that the cT phase is irrelevant to the high-$T_c$ superconductivity in the rare-Earth-doped CaFe$_2$As$_2$ system.

To check the influence of magnetic fields on the two SC phases, we measured the temperature dependence of the resistivity under different magnetic fields up to 9 T. The magnetic fields were applied along the c-axis of the single crystals. Here we show the data for one sample with $x=0.060$ (denoted as 0.060–2) in figure 4. The transition temperature of superconductivity is suppressed gradually and the transition is broadened with increasing magnetic fields. However, obvious differences for the influence of magnetic field on the two SC phases are observed. An un conspicuous field induced resistance broadening behavior is

**Figure 3.** Doping-temperature ($x$-$T$) phase diagram of Ca$_{1-x}$Nd$_x$Fe$_2$As$_2$. The data of parent phase are taken from the report by another group [12]. The regions with different colors represent the different structural phases. The two SC phases with different $T_c$ are revealed by black and blue patterns, respectively.
observed in the low-$T_c$ phase. For the high-$T_c$ phase, in contrast, the end point of the SC transition is very sensitive to the magnetic field, which shifts obviously to lower temperatures even under a magnetic field of 0.05 T. We notice that similar behaviors can be seen in the data for the Ca$_{1-x}$La$_x$Fe$_2$As$_2$ system [24]. We argue that this is a typical characteristic of Josephson weak links, which has been observed at the high-angle grain boundaries in high-$T_c$ cuprate superconductors [25, 26].

We attempted to further explore the possible origins of the non-uniform SC properties in the present system. The distribution of the Nd-dopant on a micro-scale is investigated by EDS measurements. The mapping image of Nd concentration and the chart of its distributions throughout an area of 36 $\times$ 26 $\mu$m for the sample with $x = 0.074$ are shown in figures 5(a) and (b). The spatial resolution is 1.9 $\mu$m. It shows a Nd distribution ranging from 0.061 to 0.086 and an average concentration of 0.074, which is similar to that reported on a Pr-doped CaFe$_2$As$_2$ system [20]. The full width at half maximum of the profile for the histogram in figure 5(b) is about 0.009. Our data indicate that the two-SC-phase feature observed in the present system cannot be attributed to the Nd distribution on the micro scale. Of course we cannot rule out possible heterogeneous features responsible for the non-uniform SC behaviors on a smaller scale (e.g. nano scale). It was indicated that the high-$T_c$ phase is not an interfacial

![Figure 4](image.png)

**Figure 4.** (a) Temperature dependence of resistivity with applied fields up to 9 T measured on one sample $x = 0.060-2$. (b) Field–temperature phase diagram derived from the data in panel (a).
superconductivity [23] or a filamentary-type superconductivity caused by local pinning strength and local structural defects [12, 13]. Very recently, K Gofryk et al [20] reported that the inhomogeneous and strongly localized high-$T_c$ phase is a kind of granular filamentary superconductivity emerging from clover-like regions associated with Pr dopants composed of three or four atoms in Pr-doped CaFe$_2$As$_2$. These regions with a SC gap of $\Delta \sim 30$ meV are separated and surrounded by other low-$T_c$ phases with $\Delta \sim 15$ meV and non-SC regions. So the weak-link behavior of the high-$T_c$ phase observed in our data is likely to originate from the boundaries between these high-$T_c$ regions.

4. Conclusions

In the present work, we have investigated the phase diagram and field induced resistance broadening behavior of Ca$_{1-x}$Nd$_x$Fe$_2$As$_2$ single crystals. It is found that the $c$-axis lattice parameter decreases with the increase of Nd substitution. Coexistence of two SC phases is observed. The low-$T_c$ phase exists as $x \geq 0.031$, and the high-$T_c$ phase with a $T_c$ value of about 40 K emerges when $x \geq 0.060$. The structural (T–O)/magnetic transition is found in the low Nd-doping region and totally suppressed around $x=0.060$. The new cT coexists with the high-$T_c$
phase in the same doping range. Compared to the low-$T_c$ phase, the end point of the SC transition of the high-$T_c$ phase shifts obviously to lower temperature even under a field of 0.05 T, showing a weak-link behavior. Detailed EDS measurements indicate that the non-uniform SC properties cannot be attributed to the heterogeneous Nd distribution on the micro scale.

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