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Crystal growth and phase diagram of 112-type iron pnictide superconductor \( \text{Ca}_{1-y}\text{La}_y\text{Fe}_{1-x}\text{Ni}_x\text{As}_2 \)

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Abstract

We report a systematic crystal growth and characterization of \( \text{Ca}_{1-y}\text{La}_y\text{Fe}_{1-x}\text{Ni}_x\text{As}_2 \), the newly discovered 112-type iron-based superconductor. After substituting Fe by a small amount of Ni, bulk superconductivity is successfully obtained in high-quality single crystals sized up to 6 mm. Resistivity measurements indicate common features for transport properties in this 112-type iron pnictide, suggest strong scattering from chemical dopants. Together with the superconducting transition temperature \( T_c \), and the Néel temperature \( T_N \) determined by the elastic neutron scattering, we sketch a three-dimensional phase diagram in the combination of both Ni and La dopings.

Keywords: iron-based superconductor, single crystal growth, phase diagram

(Some figures may appear in colour only in the online journal)

1. Introduction

The superconductivity (SC) discovered in iron pnictides has stimulated intensive researches in condensed matter physics since 2008 [1]. The basic structure of these materials is a stack of layered square lattices of Fe-As/Fe-P intermediate by alkali/alkali earth/rare-earth ions or oxides. So far, such ingredient has been successfully achieved in many families of iron-based superconductors, which can be classified as: 1111 (e.g. \( \text{LaFeAsO}_2 \)), 122 (e.g. \( \text{BaFe}_2\text{As}_2 \)), 111 (e.g. \( \text{LiFeAs} \)), 2131 (e.g. \( \text{Sr}_2\text{VO}_3\text{FeAs} \)), 3252 (e.g. \( \text{Sr}_2\text{Sc}_2\text{O}_3\text{Fe}_2\text{As}_2 \)), \( \text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\) (e.g. \( \text{Ca}_{10}\text{Fe}_9\text{P}_8 \)), 10-3-8 (e.g. \( \text{Ca}_{10}\text{Fe}_9\text{P}_8 \)), 1144 (e.g. \( \text{CaRbFe}_4\text{As}_4 \)), etc [2–16]. SC emerges from chemical substituted parent compounds with long-ranged antiferromagnetism (AF) or simply in stoichiometric compounds.

In 2013, SC with \( T_c \) up to 42 K in a new type iron pnictide compound \( \text{Ca}_{1-y}\text{Ln}_y\text{Fe}_4\text{As}_2 \) (Ln = La, Pr, Nd) was reported and named as 112-type iron-based superconductor [17, 18]. Although this new system contains similar elements as the tetragonal 1111, 111, and 122 families (space group \( I4/mmm \)), the crystal structure is monoclinic (space group \( P2_1 \)), with a small tilt of the whole quadrangular magnetic order, forms just below the structural transition \( T_s \), and the Néel temperature \( T_N \) determined by the elastic neutron scattering, SC emerges from chemical doping, forms just below the structural transition \( T_s \).

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doped CaFe$_2$As$_2$ [23], only filamentary SC can be found in Ca$_{1-x}$La$_x$Fe$_2$As$_2$ compound. Though the iso-valent substitution of As by Sb or post-annealing of the crystals may improve the superconducting transition and volume, it is still hard to obtain bulk SC with full Meissner shielding volume [17–19, 24]. Recently, Jiang et al have finally realized bulk SC by slightly doping Co into the ‘parent’ compound Ca$_{0.73}$La$_{0.27}$Fe$_2$As$_2$ with $T_c = 58$ K and $T_N = 54$ K [25]. Both antiferromagnetic and superconducting phases coexist microscopically with each other in the underdoped region, and optimal SC with maximum $T_c = 20$ K is obtained at 4.6% Co doping level. Surprisingly, nuclear magnetic resonance research reveals that lanthanum doping, which is generally believed to introduce electrons [2], will actually enhance $T_N$ but suppress $T_c$ simultaneously [26]. To understand the magnetism and SC in this fascinating material, it is necessary to further establish the detailed phase diagram concerning different chemical dopings both at Ca and Fe sites.

In this article, we report our results of crystal growth and characterization of Ca$_{1-x}$La$_x$Fe$_{1-y}$Ni$_y$As$_2$ with various Ni doping levels ($0 \leq x \leq 0.24$) and La doping ($y = 0.18$ and 0.24). Most of them show bulk superconductivity at the superconducting state, and systematic evolution of transport properties at the normal state. With the $T_N$ determined from neutron diffraction experiments on the single crystals and previous report [22], and $T_c$ obtained from magnetization and resistivity measurements, we establish a three-dimensional phase diagram of Ca$_{1-x}$La$_x$Fe$_{1-y}$Ni$_y$As$_2$ with rich interplay between $T_c$ and $T_N$.

2. Experiment

Ca$_{1-x}$La$_x$Fe$_{1-y}$Ni$_y$As$_2$ single crystals were grown by self-flux method using CaAs as flux [27]. Before the crystal growth, the precursors CaAs, LaAs, Fe$_{1-x}$Ni$_x$As (in nominal composition) had been prepared with raw materials Ca(Alfa Aesar, >99.5%), La(Alfa Aesar, >99.9%), Fe(Alfa Aesar, >99.5%), Ni(Alfa Aesar, >99.99%), As(Alfa Aesar, >99.99%) by solid state reaction method. For CaAs, the Ca granular and ground As chips with a ratio of 1:1 were sealed into an evacuated quartz tube and placed in a box furnace. The raw materials were heated to 400 °C slowly and held for more than 10 h, then further heated to 630 °C slowly and held for another 20 h, and finally quenched to room temperature. The mixture for the first batch was ground into powder, sealed into an evacuated quartz tube, and heated up to 670 °C again for complete reaction. For LaAs, the starting materials La and As chips were mixed with a ratio of 1:1 and loaded into an Al$_2$O$_3$ crucible and sealed into a quartz tube. The whole ampoule was slowly heated to 500 °C in 20 h, held for 10 h, then heated to 850 °C in 10 h and held for another 20 h. The Fe$_{1-x}$Ni$_x$As powders were prepared by the same method we used before [28]. All precursors were checked to be high purity crystalline phases by x-ray powder diffraction. Finally, for the Ca$_{0.82}$La$_{0.18}$Fe$_{1-y}$Ni$_y$As$_2$ samples, precursors CaAs, LaAs, Fe$_{1-x}$Ni$_x$As with a molar ratio of 3.7:0.3:1 and total mass about 10 g were ground to mix up homogeneously, then pressed into pellets, loaded into a φ21 mm × 60 mm Al$_2$O$_3$ crucible and sealed into a quartz tube with inner size φ23 mm × 100 mm. For the Ca$_{0.73}$La$_{0.27}$Fe$_{1-x}$Ni$_y$As$_2$ samples, we grow the crystals by changing the molar ratio to 1.65:0.35:1 for the corresponding precursors CaAs, LaAs, Fe$_{1-x}$Ni$_y$As. The ampoule was heated to 900 °C in 15 h and kept for 10 h first, then heated to 1180 °C in 5 h and held for 20 h for melting. At the last stage, the furnace temperature was decreased to 950 °C at a slow rate of 3 °C h$^{-1}$ and then quenched to room temperature. By cracking the melted pellet after exposing them in the air for several hours, sizable shining plate-like single crystals were successfully obtained.

To check the quality of our crystals, the crystallinity, chemical composition and planeness of cleaved surface were characterized. Single crystals x-ray diffraction (XRD) were carried out on a SmartLab 9 kW high resolution diffraction system with Cu Kα radiation (λ = 1.540 598 Å) at room temperature ranged from 5° to 90° in reflection mode. The Laue photos of the crystals were taken by a Photonic Sciences Laue camera in backscattering mode with incident beam along c-axis. The microscopic morphology and energy-dispersive x-ray spectrum (EDX) of the crystals were measured by a high resolution cold field emission scanning electron microscope (SEM) (Hitachi S-4800) equipped with an energy-dispersive x-ray spectrometer. The accurate composition of our samples were determined by the inductively coupled plasma (ICP) analysis.

The superconducting transition temperatures were determined by DC magnetization measurements on a Quantum Design Magnetic Property Measurement System with zero-field-cooling method and $H \parallel ab$ plane, where the demagnetization factor is nearly zero for the very thin crystals. The superconducting and normal state transport properties were further measured by standard four-probe resistance
measurements on a Quantum Design Physical Property Measurement System down to 2 K. Four Ohmic contacts were painted by DuPont 5025 silver paint on the crystals with contact resistance less than 1 Ω. Temperature dependence of resistivity was measured by sweeping temperature in a low rate of 1 K min⁻¹. For each doping, we measured at least three typical pieces of crystals to repeat the results.

The AF on several samples were measured by elastic neutron scattering experiments on the cold neutron triple-axis spectrometer FLEXX-V2 at BER II, Helmholtz-Zentrum Berlin in Germany. The fixed final energy was E_f = 5 meV (in wavelength λ_f = 4.05 Å) with a velocity selector before the sample and a cold Be filter after the sample. The wave vector \( \mathbf{Q} \) at \( (q_x, q_y, q_z) \) was defined as \( (H, K, L) = (q_x/a/2\pi, q_y/b/2\pi, q_z/c/2\pi) \) reciprocal lattice units by simply using the tetragonal notation where \( a \approx b \approx 3.90 \) Å and \( c \approx 10.31 \) Å. All the samples were aligned in \([H, H, 0] \times [0, 0, L]\) scattering plane, to reach the magnetic wave vector \( \mathbf{Q}_{AF} = (0.5, 0.5, L/2) \) with \( L = \pm 1, \pm 2, \pm 3, \ldots \)

3. Result and discussion

We have successfully grown two groups of Ni doped 112-type iron pnictides with different La contents: \( \text{Ca}_{0.82}\text{La}_{0.18}\text{Fe}_{1−x}\text{Ni}_x\text{As}_2 \) and \( \text{Ca}_{0.76}\text{La}_{0.24}\text{Fe}_{1−x}\text{Ni}_x\text{As}_2 \). The crystallographic results are quite similar for the two series, thus we only show typical results of the former one with La concentration \( y = 0.18 \). Figure 2(a) shows the as-grown crystals of \( \text{Ca}_{0.82}\text{La}_{0.18}\text{Fe}_{1−x}\text{Ni}_x\text{As}_2 \) with the largest size \( 5 \times 6 \times 0.5 \) mm³. All crystals have shiny surface after crashing from the ingot in the crucible. The SEM image in figure 2(b) shows the detailed characteristic of the crystal with some naturally cleaved edge along \([1, 1, 0]\) direction, as determined by x-ray Laue reflection (figure 3(c)). Figure 2(c) gives the EDX spectrum of the same crystal in figure 2(b), all elements including Ca, La, Fe, Ni, As can be detected, and their contents can be roughly estimated from the spectrum weight. To check the crystalline quality, we have performed single crystal XRD measurements on each doping level at room temperature. Five typical XRD patterns are presented in figure 3(a) for \( \text{Ca}_{0.82}\text{La}_{0.18}\text{Fe}_{1−x}\text{Ni}_x\text{As}_2 \) with \( x = 0, 0.012, 0.04, 0.1, 0.24 \). The sharp (0 0 l) peaks indicate high c-axis orientation of our crystals. No 122 phase of \( \text{Ca}_{1−x}\text{La}_{x}\text{Fe}_{2−x}\text{Ni}_x\text{As}_2 \), which has larger lattice parameter \( c \) and can be only indexed by even peaks along c-axis, has been found in all examined samples. The slightly shift of Bragg peaks toward to high 2θ angles indicates the decreasing of the length of c-axis with Ni doping level increasing, as summarized in figure 3(b). The chemical composition of our samples are characterized by ICP analysis with about 1% uncertainty. If we suppose the nominal Ni doping level \( x' \) in precursor \( \text{Fe}_{1−x'}\text{Ni}_x\text{As} \), then we have a linear relation between the real content of Ni \( x \) and the nominal one \( x' \), \( x = 0.8x' \), where the error bars in figure 3(c) come from the
statistics among 3–5 pieces of crystal in the same batch. Such segregation coefficient is same as the case of Ni doped BaFe$_2$As$_2$ [27–30], suggesting common ability of congruent melting between Fe and Ni in iron pnictides. The systematic evolution of the c-axis and real compositions prove the reliable and repeatable of our grown method. In order to compare with the previous results, we will use the real composition $x$ in the following discussion.

Figure 4 shows the temperature dependence of the DC magnetic susceptibility for Ca$_{1-y}$La$_y$Fe$_{1-x}$Ni$_x$As$_2$ single crystals. All data is normalized by the resistivity at 300 K and shifted upward with 0.3 and 0.4 one by one for (a) and (b), respectively.

Figure 5. Temperature dependence of the resistivity for Ca$_{1-y}$La$_y$Fe$_{1-x}$Ni$_x$As$_2$ single crystals. All data is normalized by the resistivity at 300 K and shifted upward with 0.3 and 0.4 one by one for (a) and (b), respectively.

Figure 6. (a), (b) The extra electrons dependence of the coefficient $A$, $B$ from the fitting $\rho(T)/\rho(300 \text{ K}) = \rho_0 + AT + BT^2$ of Ca$_{1-y}$La$_y$Fe$_{1-x}$Ni$_x$As$_2$. Inset of (b) shows the typical fitting results for Ca$_{0.82}$La$_{0.18}$Fe$_{1-x}$Ni$_x$As$_2$ with $x = 0$, 0.04 and 0.072 at normal state, where the red lines are fitting curves. (c) The extra electrons dependence of RRR of Ca$_{1-y}$La$_y$Fe$_{1-x}$TM$_x$As$_2$ (TM = Ni, Co). The extra electrons are defined as $2x + 0.63y$ for Ca$_{1-y}$La$_y$Fe$_{1-x}$Ni$_x$As$_2$ and $x + 0.63y$ for Ca$_{1-y}$La$_y$Fe$_{1-x}$Co$_x$As$_2$, respectively. The shadow areas are guides for the eyes.

superconducting transition, and the diamagnetism does not saturate at 2 K. With very little Ni doping, the superconducting transition temperature $T_c$ can be significantly improved from 25 K for $x = 0$ to 34 K for $x = 0.004$, then slowly drop down upon further Ni doping. This may indicate that this system is very close to an optimal condition for SC. More impressively, after doping more Ni, the superconducting transition width become very sharp and most of
the superconducting samples have nearly full Meissner shielding volume ($4\pi V \approx -1$) at base temperature ($T = 2$ K). Upon further doping, this system turns to be non-supercconducting over $x = 0.12$ for heavily overdoped electrons.

The normalized temperature dependence of resistivity up to 300 K $\rho(T)/\rho(300 \text{K})$ are presented in figure 5 both for Cao.82La0.18Fe1−xNi x As2 and Cao.76La0.24Fe1−xNi x As2. The systematic evolution of SC is very clear for both groups of our samples. The normal state of all dopings behaves like a metal similar to the BaFe2−xNixAs2 system [28, 30, 31]. To describe the electronic transport properties, we fit the $\rho(T)/\rho(300 \text{K})$ data by an empirical formula in the combination of linear and quadratic components: $\rho(T)/\rho(300 \text{K}) = \rho_0 + AT + BT^2$ within a wide temperature range from 30 K above the $T_N$ or $T_c$ to 300 K, which is commonly used in some cuprates, pnictides and organic superconductors [32]. Generally, the coefficient $A$ represents the non-Fermi-liquid behaviors, while the coefficient $B$ means the proportion of Fermi-liquid behaviors, and $\rho_0$ is the normalized residual resistivity. In this way, we can also obtain the residual resistivity ratio $\text{RRR} = \rho(300 \text{K})/\rho(0 \text{K}) = 1/\rho_0$ related to the strength of impurity scattering. For both cases with $y = 0.18$ and $0.24$, such fitting agrees very well up to 300 K. Similarly, we can calculate the magnitude of $\text{RRR}$ in Cao.74La0.26Fe1−xCo x As2 and Cao.8La0.2Fe0.98Co0.02As2 compounds reported before [25, 33]. By simply considering both La and Ni/Co dopants contribute electrons into the system, e.g., the DMFT calculation indicates 0.17 e/Fe in the Fe2As2 layer for Cao.73La0.27FeAs2 compound [22], we could unify the electron doping level to be extra electrons, with 0.63 e/Fe per La and 2 e/Fe per Ni or 1 e/Fe per Co. Here, the value of extra

![Figure 7. Neutron diffraction experiments on Ca1−yLa yFe1−xNi x As2 single crystals. (a)–(c) Magnetic Bragg peaks by scanning $Q$ along [H, H, H] direction for $x = 0$, $y = 0.18$ and $x = 0.024$, $y = 0.18$; $x = 0$, $y = 0.24$; $x = 0.024$, $y = 0.24$. The solid lines in the figures are gauss fittings of the data. (d)–(f) Temperature dependence of the magnetic scattering at $Q_{\text{AF}} = (0.5, 0.5, 0.5)$ for the corresponding doping in (a)–(c). The antiferromagnetic phase transition temperature $T_N$ is marked by the black arrows.](image-url)
In summary, high-quality sizable single crystals of Ca$_{1-x}$La$_x$Fe$_1-y$Ni$_y$As$_2$ have been grown successfully by the self-flux method. Transport behaviors at normal state can be simply described by doped extra electrons in the 112-type families. The detailed phase diagram shows that bulk SC can be introduced by Ni doping above $x = 0.004$ after suppressing the long-ranged AF order. Although the La doping have weak effect on the Néel temperature of Ni-free Ca$_{1-x}$La$_x$Fe$_2$As$_2$, larger co-existing regime between SC and AF, but slightly narrower superconducting dome are obtained for $y = 0.24$ system rather than $y = 0.18$ case, maybe due to stronger impurity scattering.

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