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FAST TRACK COMMUNICATION

Superconductivity above 33 K in (Ca_{1-x}Na_x)Fe₂As₂

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Abstract

We report the synthesis of (Ca_{0.33}Na_{0.66})Fe₂As₂ showing a superconducting transition with T_c above 33 K. Both dc magnetic susceptibility or specific heat measurements indicated the bulk superconductivity nature of the sample. We also have successfully grown single crystals of the (Ca_{0.33}Na_{0.66})Fe₂As₂ superconductors. The single crystals exhibit sharp superconducting transitions with T_c above 33 K. The effects of magnetic field on the superconducting transitions are studied, giving rise to high upper critical fields with $H_{c2}^c \approx 85$ T and $H_{c2}^{ab} \approx 172$ T, respectively. The anisotropy parameter was calculated to be around 2.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the discovery of the iron-arsenide-based superconductor LaFeOAs with superconducting transition temperature (T_c) 26 K [1] a series of new pnictide superconductors were found including RFeAs (OF), called the '1111' type where R is a rare earth element, AFe₂As₂, called the '122' type where A is an alkaline earth element or AFeAs, called the '111' type where A is an alkaline metal [2–8]. All these iron-based superconductors crystallize into structures containing 'FeAs' layers where the superconductivity takes place. The high T_c makes iron-based superconductors the second family next to copper oxide superconductors. It is believed that magnetism is usually harmful to superconductivity so that superconductors should be free of magnetic elements typically like iron. The superconductivity with very high T_c in iron pnictide superconductors has attracted world-wide attention either for their unconventional superconducting mechanism or the prospects for applications [9]. Like high T_c cuprates the superconductivity of iron pnictides developed from the magnetically ordered parent state wherein the Fe ion forms a spin density wave state (SDW) [10, 11]. Superconductivity can be induced either via chemical doping or pressure that generate electrical carriers to the iron plane while suppressing the SDW state.

Among iron-based superconductors, the '122' system has been extensively investigated since the compounds are

relatively stable while large size single crystals can be grown that are very important for mechanism studies. The alkaline-earth-based AFe₂As₂ (where A is Ca, Sr or Ba) are the typical '122' parent compounds. Superconductivity can be generated by introducing carriers into the iron layer through heterovalence substitution of monovalence alkaline metal to bivalence alkaline earth metal. The Ba_{0.6}K_{0.4}Fe₂As₂ is the first reported '122' superconductor with T_c up to 38 K [6]. Similar results were obtained for Sr_{0.6}K_{0.4}Fe₂As₂ with $T_c \sim 35$ K [12]. But for Ca122 the chemical doping at the Ca site resulted in a superconducting transition with $T_c \sim 26$ K [13] for Ca_{0.6}Na_{0.4}Fe₂As₂ or T_c 20 K [14] for Ca_{0.5}Na_{0.5}Fe₂As₂. The reason for using sodium instead of potassium dopant for CaFe₂As₂ is that the ionic size of Na¹⁺ (1.18 Å) matches that of Ca²⁺ (1.12 Å) [15]. Comparing the superconducting transitions of the aforementioned three alkaline earth '122' superconductors, the (Ca, Na)122 is around 10 K lower than that for (Ba, K)122 or (Sr, K)122. Here we report that a superconducting transition with T_c above 33 K can be obtained in (Ca, Na)122 compounds. Our results suggest that high T_c can be achieved with higher Na doping. A maximum T_c above 33 K was realized for (Ca_{0.33}Na_{0.66})Fe₂As₂ corresponding to a two-thirds nominal doping of Na at the A site. The studies on the single-crystal samples give rise to relatively lower anisotropy.

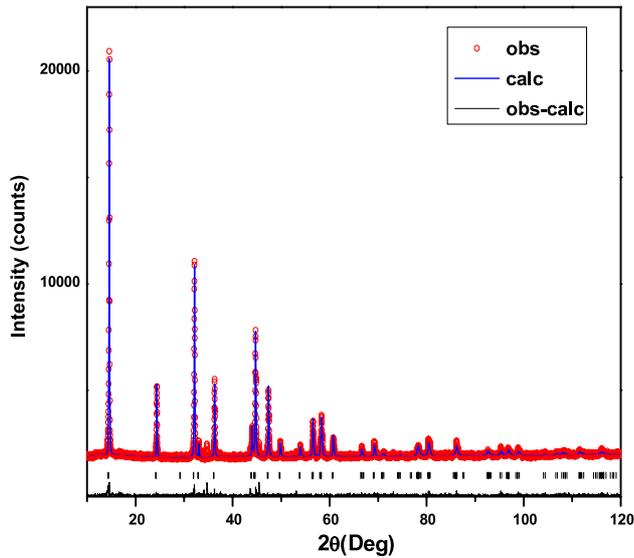


Figure 1. The Rietveld refinements of x-ray diffraction of $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ polycrystals showing the single-phase nature of 122 structure.

2. Experimental details

The $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ polycrystals are synthesized using the solid state reaction method. Here we show that using CaAs or Na_3As precursors instead of Ca or Na elements helps greatly in achieving a homogeneous reaction with increased Na content since the alkaline or alkaline earth metals are very volatile at high temperatures. The CaAs precursor was synthesized from the mixtures of high purity Ca granular plus arsenic powder sealed in an evacuated quartz tube that is sintered at 850°C for 30 h. The Na_3As precursor was sintered using a similar method but with a sintering temperature of 600°C . The starting materials of CaAs, Na_3As , FeAs and high purity Fe powders were mixed according to nominal composition $(\text{Ca}_{1-x}\text{Na}_x)\text{Fe}_2\text{As}_2$. The samples are initially synthesized at high pressure (2 GPa) and high temperature (800°C) for 30 min in order to suppress component evaporation. To get the single phase we further synthesized samples at ambient pressure that are studied in this work. The mixtures are sealed in an evacuated titanium tube that is in turn sealed in an evacuated quartz tube. The mixed starting materials are heated to 800°C at 3°C min^{-1} where it is kept for 30 h before slowly decreasing to room temperature at a rate 2°C min^{-1} . The sintered materials are ground with several repeat processes in order to have homogeneous samples. The highest sodium content with a single-phase nature is up to a nominal composition of $(\text{Ca}_{1/3}\text{Na}_{2/3})\text{Fe}_2\text{As}_2$ that shows the maximum superconducting transition with T_c above 33 K. We therefore focus on $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ in this work. The $(\text{Ca}, \text{Na})\text{Fe}_2\text{As}_2$ single crystals are grown using the self-flux method. The precursor materials are Na_3As , CaAs and FeAs that are mixed with Fe powders with nominal composition $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$. The mixtures are loaded into an evacuated alumina tube with 99% purity before sealing in an Nb tube. The Nb tube is in turn sealed

Table 1. The structural details of $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$. (Note: space group: $I4/mmm$. Unit-cell dimensions: $a = b = 3.841 \text{ \AA}$; $c = 12.2 \text{ \AA}$ $R_{wp} = 3.56\%$, $R_p = 2.89\%$. The refinement range of 2θ is 10° – 120° . Cu $\text{K}\alpha_1$ radiation was used.)

Atom	Site	X	Y	Z	Occupancy
Na/Ca	2a	0	0	0	0.66/0.33
Fe	4d	0	0.5	0.25	1
As	4e	0	0	0.3648	1

in an evacuated quartz tube. All the processes of material mixing or grinding are conducted with the protection of Ar atmosphere in a glove box. The mixtures are first heated to 800°C at 3°C min^{-1} to initially react the composition for 10 h, followed by further heating up to 1100°C with a rate of 3°C min^{-1} . The samples are kept at 1100°C for 10 h followed by a slow decrease to 800°C at a rate of $0.1^\circ\text{C min}^{-1}$ in order to grow single crystals. The obtained single crystals are in shiny platelets of 3 mm size in the ab plane. The compositions of the single crystals or the polycrystals are analyzed using energy-dispersive spectroscopy (EDX). The detected $\text{Na}/(\text{Ca} + \text{Na})$ ratio is 0.66 ± 0.03 , in general agreement with the nominal composition. This is ascribed to the use of CaAs or Na_3As precursors as Ca or Na source materials, which effectively avoided the evaporation of these metal elements during high temperature reactions. The recovered samples are characterized by x-ray powder diffraction with a Philips X'pert diffractometer using Cu $\text{K}\alpha_1$ radiation. Diffraction data are collected at 0.02° and 15 s/step . Rietveld analyses are performed by using the GSAS software package. The dc magnetic susceptibility is characterized using a SQUID magnetometer (Quantum Design) while the electric conductivity as well as the specific heat are measured using the standard four-probe method with a PPMS system.

3. Results

Figure 1 shows the x-ray diffraction pattern of the sample with nominal composition $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$. The Rietveld refinement indicated a single-phase nature of the 122 structure with tetragonal lattice parameters of 3.841 \AA and 12.2 \AA for a and c , respectively, as shown in table 1. Comparing with the parent compound CaFe_2As_2 , the a axis shrank, indicating the hole doping nature [13], while the c axis expanded since the ionic radius of Na^{1+} (1.18 \AA) is larger than that for Ca^{2+} (1.12 \AA) [15]. Figure 2(a) shows the magnetization measurements of the polycrystal $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ sample in both ZFC or FC mode at 30 Oe with a very sharp superconducting transition above 33 K. The superconducting volume fraction is roughly estimated to be $>30\%$ at 5 K based on the FC signal, indicating the bulk nature. This is verified by specific heat measurement as shown in figure 2(b), where a jump at T_c clearly indicates the bulk superconducting nature of the sample. Fitting the low temperature specific data above T_c using the formula $C = \gamma T + \beta_3 T^3$ gives rise to the electronic specific coefficient $\gamma = 17.262 \text{ mJ mol}^{-1} \text{ K}^{-2}$. The result suggests the mass enhancement of carriers due to electron correlation. To further investigate intrinsic properties

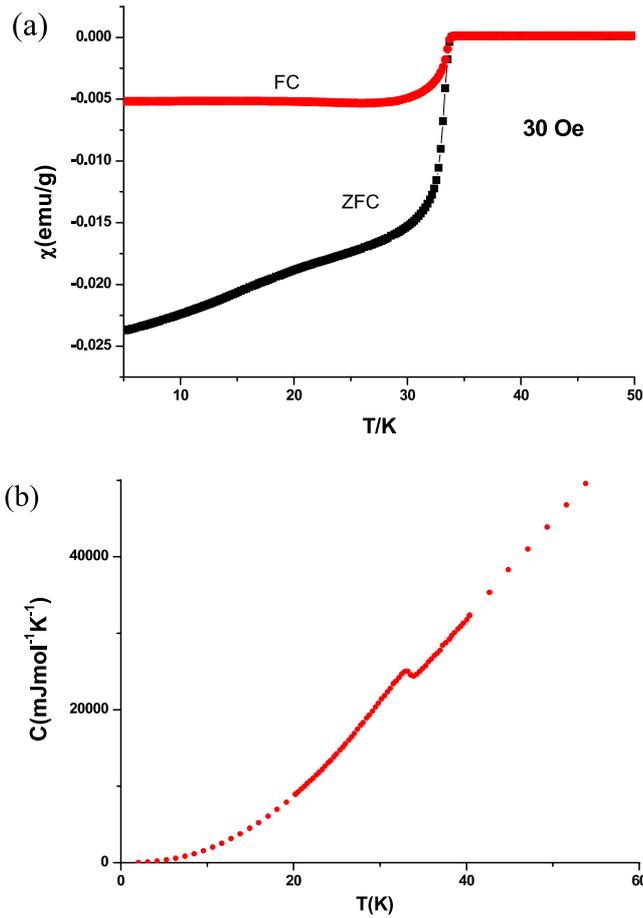


Figure 2. (a) Temperature-dependent magnetization of $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ superconductors at both ZFC and FC conditions with $H = 30$ Oe, showing the superconducting transition above 33 K; (b) the specific heat of $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ superconductors, indicating the superconducting transition above 33 K.

of this high T_c $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ phase we measured the anisotropy of the single crystal. The single crystals are stable in air. This is, however, quite different from the ‘111’-type NaFeAs that is very hygroscopic in air from our previous experiences [16]. The superconducting transition of $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ single crystals is very sharp, with a transition width less than 1 K as shown in figures 3(a) and (b). The high T_c superconductivity may be related to the geometry optimization of FeAs coordination, especially the height of As to the Fe layer [17]. The single-crystal behavior is like a metal at the normal states with the ratio of residual resistance (RRR) ~ 6 , indicating the high quality of the superconducting single crystals.

The effects of magnetic field on the superconducting transition are investigated with H either parallel ($H_{\parallel ab}$) or perpendicular ($H_{\parallel c}$) to the ab plane of a single crystal. The sharp superconducting transitions imply higher upper critical fields. It is clear that the effect is larger for $H_{\parallel c}$ than that for $H_{\parallel ab}$. The upper critical field H_{c2} was determined using the middle point of the superconducting transition. It is shown that the critical field determined using this method is a rough estimation because of the vortex effects. Figure 3(c) shows H_{c2} as a function of temperature. The slopes of the

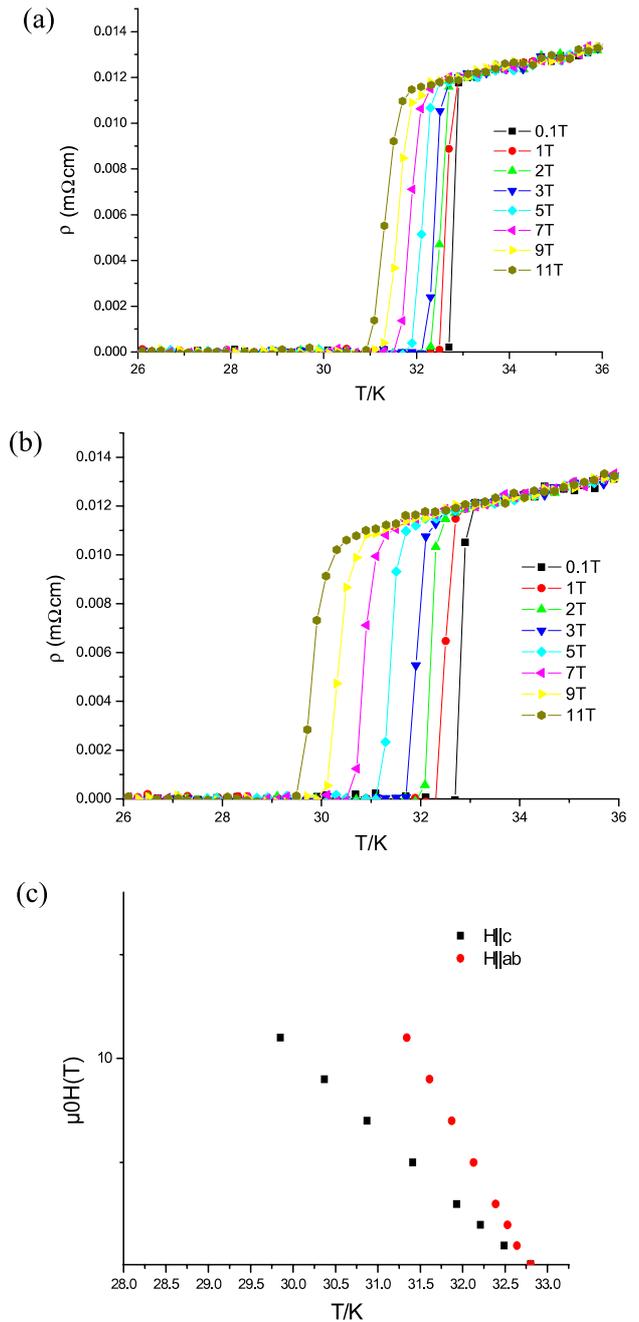


Figure 3. (a) The superconducting transition of $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ single crystal in magnetic fields $H_{\parallel ab}$. (b) The superconducting transition of $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ single crystal in magnetic fields $H_{\parallel c}$. (c) Upper critical fields of superconducting $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ single crystal with $H_{\parallel ab}$ or $H_{\parallel c}$.

curves at $dH_{c2}/dT|_{T=T_c}$ are determined to be 3.73 T K^{-1} and 7.53 T K^{-1} for $H_{\parallel c}$ and $H_{\parallel ab}$, respectively. Taking 33 K T_c , based on the Werthamer–Helfand–Hohenberg (WHH) formula of $H_{c2}(0) = -0.693(dH_{c2}/dT)T_c$, the upper critical fields are calculated to be 85 T and 172 T for $H_{c2}^c(0)$ and $H_{c2}^{ab}(0)$, respectively. Consequently, the anisotropy parameter $\gamma = H_{c2}^{ab}/H_{c2}^c$ is calculated to be ≈ 2 , indicating a low anisotropy of the $(\text{Ca}_{0.33}\text{Na}_{0.66})\text{Fe}_2\text{As}_2$ single crystal. The anisotropy parameter γ is comparable to that for other 122 single crystals. This is particularly consistent with the

results reported by Yuan *et al* [18] on the (BaK)Fe₂As₂ single crystal where nearly isotropic superconductivity with $\gamma \approx 1-2$ was observed. So far there are several reports on a superconducting sodium-doped Ca122 system including high pressure synthesized (Ca_{0.6}Na_{0.4})122 with T_c 26 K [13] or (Ca_{0.5}Na_{0.5})122 with T_c 20 K [14]. The present work indicated that higher T_c can be achieved for high Na-doped Ca122 superconductors. Comparing with the optimally doped (Ba_{0.6}K_{0.4})Fe₂As₂ with nominal carrier density 0.2/Fe [6], this high T_c (Ca_{0.33}Na_{0.66})Fe₂As₂ is 'over-doped' with an average carrier density 0.33/Fe. The present work raises an interesting question: how do we comprehensively understand the correlation of the superconducting transition temperature with carrier density for the Ca122 compounds? Although our preliminary experimental results from EDX indicated the chemical compositions of the synthesized (Ca_{0.33}Na_{0.66})Fe₂As₂ polycrystals or single crystals are consistent with the nominal composition, deep investigations using neutron experiments will be needed to more accurately determine the chemical composition in the crystals. In this context it would be interesting to study what kind of electronic structures are responsible for the high T_c superconductivity for (Ca_{0.33}Na_{0.66})Fe₂As₂.

In summary we have successfully observed superconductivity with T_c above 33 K in (Ca_{0.33}Na_{0.66})Fe₂As₂. The higher Na doping makes (Ca, Na)122 superconductive with T_c similar to those for (Ba, K)Fe₂As₂ or (Sr, K)Fe₂As₂, which invokes extended studies on the correlation between superconducting transition temperature and doping level. The single crystal shows an anisotropy of about 2, which is consistent with the previously reported other 122 superconductors.

Acknowledgments

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References

- [1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Am. Chem. Soc.* **130** 3296
- [2] Chen X H, Wu T, Wu G, Liu R H, Chen H and Fang D F 2008 *Nature* **453** 761
- [3] Chen G F, Li Z, Wu D, Li G, Hu W Z, Dong J, Zheng P, Luo J L and Wang N L 2008 *Phys. Rev. Lett.* **100** 247002
- [4] Ren Z-A, Yang J, Lu W, Yi W, Shen X-L, Li Z-G, Che G-C, Dong X-L, Sun L-L, Zhou F and Zhao Z-X 2008 *Europhys. Lett.* **82** 57002
- [5] Wen H H, Mu G, Fang L, Yang H and Zhu X Y 2008 *EuroPhys. Lett.* **82** 17009
- [6] Rotter M, Tegel M and Johrendt D 2008 *Phys. Rev. Lett.* **101** 107006
- [7] Hsu F-C, Luo J-Y, Yeh K-W, Chen T-K, Huang T-W, Wu P M, Lee Y-C, Huang Y-L, Chu Y-Y, Yan D-C and Wu M-K 2008 *Proc. Natl Acad. Sci. USA* **105** 14262
- [8] Wang X C, Liu Q Q, Lv Y X, Gao W B, Yang L X, Yu R C, Li F Y and Jin C Q 2008 *Solid State Commun.* **148** 538
- [9] Ishida K, Nakai Y and Hosono H 2009 *J. Phys. Soc. Japan* **78** 062001
- [10] de la Cruz C, Huang Q, Lynn J W, Li J, Ratcliff W, Zarestky J L, Mook H A, Chen G F, Luo J L, Wang N L and Dai P 2008 *Nature* **453** 899
- [11] Zhao J, Adroja D T, Yao D-X, Bewley R, Li S, Wang X F, Wu G, Chen X H, Hu J and Dai P 2009 *Nat. Phys.* **5** 555
- [12] Chen G F, Li Z, Li G, Hu W Z, Dong J, Zhang X D, Zheng P, Wang N L and Luo J L 2008 *Chin. Phys. Lett.* **25** 3403
- [13] Shirage P M, Miyazawa K, Kito H, Eisaki H and Iyo A 2008 *Appl. Phys. Express* **1** 081702
- [14] Wu G, Chen H, Wu T, Xie Y L, Yan Y J, Liu R H, Wang X F, Ying J J and Chen X H 2008 *J. Phys.: Condens. Matter* **20** 422201
- [15] Shannon R D 1976 *Acta Crystallogr. A* **32** 751
- [16] Wang X C, Liu Q Q, Yang L X, Deng Z, Lv Y X, Gao W B, Zhang S J, Yu R C and Jin C Q 2009 *Front. Phys. China* **4** 464
- [17] Mizuguchi Y, Hara Y, Deguchi K, Tsuda S, Yamaguchi T, Takeda K, Kotegawa H, Tou H and Takano Y 2010 arXiv:1001.1801
- [18] Yuan H Q, Singleton J, Balakirev F F, Baily S A, Chen G F, Luo J L and Wang N L 2009 *Nature* **457** 565