Annealing effects on superconductivity in SrFe$_{2-x}$Ni$_x$As$_2$

S. R. Saha, N. P. Butch, K. Kirshenbaum, Johnpierre Paglione

Center for Nanophysics and Advanced Materials, Department of Physics, University of Maryland, College Park, MD 20742, USA

Abstract

Superconductivity has been explored in single crystals of the Ni-doped FeAs-compound SrFe$_{2-x}$Ni$_x$As$_2$ grown by self-flux solution method. The antiferromagnetic order associated with the magnetostructural transition of the parent compound SrFe$_2$As$_2$ is gradually suppressed with increasing Ni concentration $x$ and bulk-phase superconductivity with full diamagnetic screening is induced near the optimal doping of $x = 0.15$ with a maximum transition temperature $T_c \sim 9.8$ K. An investigation of high-temperature annealing on as-grown samples indicate that the heat treatment can enhance $T_c$ as much as $\sim 50\%$.

Key words: superconductivity, iron-pnictides, annealing, SrFe$_{2-x}$Ni$_x$As$_2$

The discovery of high-temperature superconductivity in new iron-based pnictide compounds has attracted much recent attention [1]. Suppression of the magnetic/structural phase transition, either by chemical doping or high pressure, is playing a key role in stabilizing superconductivity in the ferropnictides. Oxygen-free FeAs-based compounds with the ThCr$_2$Si$_2$-type (122) structure exhibit superconductivity with $T_c$ as high as 25 K by partial substitution of Fe with other transition metal elements, e.g., BaFe$_{2-x}$Co$_x$As$_2$ [2, 3], SrFe$_{2-x}$Co$_x$As$_2$ [4], BaFe$_{2-x}$Ni$_x$As$_2$ [5, 6], SrFe$_{2-x}$M$_x$As$_2$ (M= Rd, Ir, and Pd) [7]. Interestingly, in BaFe$_{2-x}$Co$_x$As$_2$ [2, 3] and SrFe$_{2-x}$M$_x$As$_2$ [4], the maximum $T_c$ is found at $x = 0.15$, whereas in BaFe$_{2-x}$Ni$_x$As$_2$, the maximum $T_c$ occurs at approximately $x = 0.10$ [6, 7], suggesting that Ni substitution may indeed contribute twice as many $d$-electrons to the system as Co.

We have synthesized and studied single-crystalline SrFe$_{2-x}$Ni$_x$As$_2$ and found that Ni substitution induces bulk superconductivity. Contrary to expectations framed by prior studies of similar compounds [3, 4, 6, 7], we observe a relatively low maximal $T_c$ value of $\sim 10$ K in this series, centered at a Ni concentration approximately half that of the optimal Co concentration in SrFe$_{2-x}$Co$_x$As$_2$ [5]. We have investigated the effect of high-temperature annealing on as grown samples. Interestingly, annealing causes an enhancement of $T_c$ as much as $\sim 50\%$.

Single-crystalline samples of SrFe$_{2-x}$Ni$_x$As$_2$ were grown using the FeAs self-flux method [11]. The FeAs and NiAs binary precursors were first synthesized by solid-state reaction of (99.999% pure) Fe/Ni powder with (99.99% pure) As powders. Then FeAs and NiAs were mixed with elemental (99.95% pure) Sr in the ratio $4 - 2x:2x:1$ in an alumina crucible and heated in a quartz tube sealed in a partial atmospheric pressure of Ar to 1200°C. Crystals were characterized by X-ray diffraction and wavelength-dispersive X-ray spectroscopy (WDS). Resitivity ($\rho$) was measured with the standard four-probe ac method in a commercial PPMS and magnetic susceptibility ($\chi$) was measured in a commercial SQUID magnetometer.

Figure 1: (a) Temperature dependence of in-plane electrical resistivity in SrFe$_2$As$_2$ and SrFe$_{1.85}$Ni$_{0.15}$As$_2$ normalized to 300 K. (b) Temperature dependence of magnetic susceptibility $\chi$ in SrFe$_2$As$_2$ and SrFe$_{1.85}$Ni$_{0.15}$As$_2$ for zero-field-cooling (ZFC). The arrows indicate the position of $T_0$ (defined in the text).

Figure (a) presents the comparison of the in-plane resistivity $\rho(T)$ between two typical single crystals of SrFe$_2$As$_2$ and SrFe$_{1.85}$Ni$_{0.15}$As$_2$. As shown, $\rho(T)$ data for SrFe$_2$As$_2$ decreases with temperature from 300 K like a metal and then exhibits a sharp kink at $T_0 = 198$ K, where a structural phase transition (from tetragonal to orthorhombic upon cooling) is known to coincide with the onset of antiferromagnetic (AFM) order [9]. Below $T_0$, $\rho$ continues to decrease without any trace of superconductivity down to 1.8 K. In many undoped SrFe$_2$As$_2$ samples, strain-induced superconductivity with $T_c = 21$ K has been
observed \[10\]. However, here we present \(x = 0\) data for a sample with all traces of superconductivity removed by heat treatment. For \(x = 0.15\), which is close to optimal doping, the anomaly associated with \(T_0\) is suppressed and transformed into a smooth minimum around 37 K. The minimum, and hence \(T_0\), disappears for \(x > 0.15\), leading to a maximum \(T_c \sim 9.8\) K and a dome-like superconducting phase diagram \[1\]. Figure \[1b\] presents the temperature dependence of the in-plane magnetic susceptibility \(\chi\) in SrFe\(_2\)As\(_2\) and SrFe\(_{1.85}\)Ni\(_{0.15}\)As\(_2\) crystals. The overall behavior of \(\chi(T)\) for \(x = 0\) shows a modest temperature dependence interrupted by a sharp drop at \(T_0\). The low-field \(\chi(T)\) data at low temperatures presented here does not show any increase like that in Ref. \[9\], indicating both good sample quality (\textit{i.e.}, minimal magnetic impurity content) and no indication of strain-induced superconductivity \[10\]. For \(x = 0.15\), the large step-like feature at \(T_0\) disappears and bulk superconductivity is induced (clearly shown in Fig. 2).

![Figure 2: Volume magnetic susceptibility in SrFe\(_{1.85}\)Ni\(_{0.15}\)As\(_2\) sample measured before (circles) and after annealing a sample at 700°C for 7 days (squares), 14 days (diamonds), and 28 days (triangles). The lines are guides through the data points. The inset shows the annealing time dependence of \(T_c\) for this sample (filled triangles). The enhancement of \(T_c\) in a second piece of sample annealed for 1 day is also plotted (filled squares).](image)

We have investigated the effect of high temperature annealing on single crystals of SrFe\(_{2-\delta}\)Ni\(_{1-x}\)As\(_2\) and found a rather dramatic 10-50% enhancement in the value of \(T_c\). This enhancement is reflected in the full diamagnetic screening and is therefore a bulk phenomenon. Figure \[2\] shows the effect of annealing on the superconducting transition detected in \(\chi(T)\) of one SrFe\(_{1.85}\)Ni\(_{0.15}\)As\(_2\) annealed at 700°C after wrapping with Ta foil and sealing in a quartz tube under partial atmospheric pressure of Ar. Annealing for 7 and 14 days enhances the \(T_c\) (onset) from \(\sim 6.2\) in the as-grown sample to \(\sim 8.9\) K and \(\sim 9.2\) K, respectively, with the sharpening of the transition. Annealing for 21 and 28 days does not enhance the \(T_c\) further, while it gradually reduces the superconducting volume fraction, indicating 14 days as the optimal annealing time. The inset shows the annealing time dependence of \(T_c\). Enhancement of \(T_c\) due to annealing of as-grown SrFe\(_{2-\delta}\)Ni\(_{1-x}\)As\(_2\) (for several values of \(x\)) for 1 day at 700°C has been found both in \(\rho(T)\) and \(\chi(T)\) measurements \[1\]. Such an enhancement of \(T_c\) could be an indication of improved crystallinity due to release of residual strain, and/or improved microscopic chemical homogeneity of Ni content inside the specimens, thereby optimizing the stability of superconductivity.

A similar annealing effect was reported in LnFeOP (Ln=La, Pr, Nd) single crystals, where a heat treatment in flowing oxygen was also found to improve superconducting properties \[11\]. It is further noteworthy to report that some as-grown crystals of SrFe\(_{2-\delta}\)Ni\(_{1-x}\)As\(_2\) for \(x < 0.16\) (except \(x = 0.10\)) show what looks to be a partial superconducting transition near 20 K that is completely removed by heat treatment \[1\]. Although it is tempting to posit that 20 K is a possible value for optimal \(T_c\) in this series of Ni-substituted compounds, note that aside from the enhancement of \(T_c\) as mentioned above, the removal of this feature is the only change observed in measured quantities imposed by annealing: neither the normal state resistivity nor magnetic susceptibility show any change after annealing. Furthermore, susceptibility does not show any indication of diamagnetic screening in the as-grown samples at 20 K. Because the 20 K kink is removed with heat treatment, and, moreover, is always found to be positioned near the same temperature, we believe this feature may be connected to the strain-induced superconductivity found in undoped SrFe\(_2\)As\(_2\) \[10\]. However, note that only a mild 5 minute heat treatment of 300°C removes the partial volume superconductivity in SrFe\(_2\)As\(_2\), while a substantially higher temperature (700°C) is required to remove this feature in SrFe\(_{2-\delta}\)Ni\(_{1-x}\)As\(_2\). If the two phenomena are related, it is possible that internal strain is stabilized by the chemical inhomogeneity associated with transition metal substitution in SrFe\(_{2-\delta}\)Ni\(_{1-x}\)As\(_2\) thus requiring higher temperatures to remove. More systematic studies of the effect of annealing on SrFe\(_{2-\delta}\)Ni\(_{1-x}\)As\(_2\) are under way to investigate the microscopic change in the sample.

In summary, single crystals of the Ni-substituted series SrFe\(_{2-\delta}\)Ni\(_{1-x}\)As\(_2\) were successfully synthesized. The magnetoostructural order is suppressed and bulk superconductivity arises near the optimal doping \(x = 0.15\) with a \(T_c\) value reaching as high as \(\sim 9.8\) K. Interestingly, annealing treatments of as-grown single crystals result in a rather strong enhancement of the superconducting transition across this range of \(x\), with \(~ 50\%\) increase in \(T_c\) values for \(x = 0.15\) for an optimal annealing time of 14 days.

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