Iron isotope effect in the iron arsenide superconductor (Ca$_{0.4}$Na$_{0.6}$)Fe$_2$As$_2$

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Abstract. We report a new sample synthesis technique for polycrystalline (Ca$_{1-x}$Na$_x$)Fe$_2$As$_2$ ($0 < x \leq 0.6$) and measurements of an iron isotope effect in optimally doped (Ca$_{0.4}$Na$_{0.6}$)Fe$_2$As$_2$ with three types of iron isotopes ($^{54}$Fe, natural Fe, and $^{57}$Fe). We synthesized isotope samples carefully not to give rise to a difference in the Na content $x$ between different isotope samples, which becomes potentially a factor for an extrinsic difference in the superconducting transition temperature $T_c$ between those samples. No significant difference in lattice parameters between those samples is shown by measurements of powder x-ray diffraction (XRD), implying that the Na content in samples is well-controlled. Our estimate of the iron isotope coefficient $\alpha_{Fe}$ defined by $-\frac{d \ln T_c}{d \ln M_{Fe}}$, where $M_{Fe}$ is the iron isotope mass, is -0.19. These indicate that in (Ca$_{0.4}$Na$_{0.6}$)Fe$_2$As$_2$, the iron isotope coefficient becomes definitely negative. We discuss the implications of this fact, considering previous measurements of an iron isotope effect in different iron-based superconductors.

1. Introduction

The recent discovery of superconductivity at 26 K in LaFeAsO$_{1-x}$F$_x$ [1] inspired an effort to find a new high-temperature superconductor containing iron, followed by finding of a new class of high-temperature superconductors, the so-called iron-based superconductors. The highest superconducting transition temperature $T_c$ in iron-based superconductors has reached to 56 K until now [2]. Whether the mechanism of superconductivity in iron-based superconductors is identified with the conventional phonon mechanism or not is a matter for argument. Several studies [3-5] suggest that superconductivity at the high $T_c$ cannot be explained by conventional electron-phonon interactions but antiferromagnetic spin fluctuations, which evokes an analogy between cuprates and iron-based superconductors. However cuprates are much more anisotropic and have $d$-wave gap symmetry, while iron-based superconductors show primarily $s$-wave gap symmetry (conventional superconductors have typically $s$-wave gap symmetry) [6-8]. We are still uncertain about the mechanism of superconductivity in iron-based superconductors. In order to investigate the implications of electron-phonon interactions for the mechanism of superconductivity, it is helpful to study an isotope effect on $T_c$. The isotope coefficient $\alpha$ defined by $-\frac{d \ln T_c}{d \ln M}$, where $M$ is the isotope mass, is 0.5 in conventional superconductors in principle, actually depending on Coulomb interactions between...
electrons. In many simple metals like Hg, Pb, and Zn, isotope coefficients are found to be nearly 0.5. For a binary alloy superconductor, MgB$_2$ ($T_c$=40 K), $\alpha$ of 0.3 is found in a boron isotope effect study [9]. It demonstrates that the electron pairing is primarily phonon-mediated in MgB$_2$, though the mechanism was argued owing to relatively higher $T_c$ than in conventional superconductors. For iron-based superconductors, several groups have reported on an iron isotope effect. Shirage and co-workers show that $\alpha_{Fe}$=-0.08 [10] and -0.24 [11] in (Ba$_{0.6}$K$_{0.4}$)Fe$_2$As$_2$ ($T_c$=38 K) and SmFeAsO$_{1-x}$ ($T_c$=54 K), respectively. Tsuge and co-workers [12] show $\alpha_{Fe}$=-0.54 in FeSe$_{1-x}$Te$_x$ ($x=0.65$), i.e, the so-called inverse isotope effect. On the other hand, Liu and co-workers [13] show that $\alpha_{Fe}$=0.37 and 0.34 in (Ba$_{0.6}$K$_{0.4}$)Fe$_2$As$_2$ ($T_c$=38 K) and SmFeAsO$_{1-x}$Fe$_x$ ($T_c$=42 K), respectively. Khasanov and coworkers [14] report $\alpha_{Fe}$=0.81 in FeSe$_{1-x}$Fe. There are non-negligible discrepancies in $\alpha_{Fe}$ values between measurements for compounds of the same type. Since $T_c$ of these superconductors strongly depends on differences in the K content, O content, Te content, or Se content, the reason for the discrepancies might be such a compositional difference between isotope samples synthesized separately. Thus, in different iron-based superconductors, we would like to investigate the iron isotope effect for isotope samples all of which have no difference in the composition.

In this paper, we show a new sample synthesis technique for polycrystalline (Ca$_{0.7}$Na$_{0.3}$)Fe$_2$As$_2$ (0<x<0.6) not to give rise to a difference in the Na content $x$ and measurements of the iron isotope effect on $T_c$ in samples synthesized by this technique. A negative isotope effect has been definitely observed by using several sets (S1, S2, and S3) of three iron isotope samples ($^{54}$Fe, natural Fe, and $^{57}$Fe). We discuss the implications of this fact, considering the previous measurements of the iron isotope effect mentioned above.

2. Experimental

We used three types of Fe: $^{54}$Fe enriched powder (ISOFLEX USA, purity 99.99%, $M_{Fe}$=54.01), $^{57}$Fe enriched powder (ISOFLEX USA, purity 99.99%, $M_{Fe}$=57.00), and natural Fe powder ($M_{Fe}$=55.85, including 5.8% of $^{54}$Fe, 91.8% of $^{56}$Fe, and 2.1% of $^{57}$Fe). In a new technique, precursors of CaAs, NaAs, and As powder were mixed and divided into two or three equal weights, resulting in two or three mixed precursors with the same Na content. Then the mixed precursors were mixed with $^{54}$Fe, $^{57}$Fe and natural Fe powder respectively. The mixtures were pressed into pellets. The two pellets were sandwiched with other two (Ca$_{0.7}$Na$_{0.3}$)Fe$_2$As$_2$ pellets with natural Fe. These pellets were put into a sealed stainless steel tube and then heated at 750°C for 24 h. The Na content in samples is decreased somewhat by vaporization of Na. However, Na vaporized in outer pellets can compensate the loss of the Na content in samples. Powder x-ray diffraction measurements were carried out by using CuK$_{α}$ radiation. All the samples have a single phase and differences in lattice parameters between two samples synthesized simultaneously are negligible. The unit cell lattice parameters of both samples

![Temperature dependence of magnetic susceptibility for S1 isotope samples ($^{54}$Fe and $^{57}$Fe) of (Ca$_{0.7}$Na$_{0.3}$)Fe$_2$As$_2$. The susceptibility is normalized by its value at 5 K. The data of the $^{54}$Fe and $^{57}$Fe samples are shown by circular and square symbols. The inset shows the determination of $T_c$. The natural Fe data almost overlaps the $^{57}$Fe data, so that it is not shown here.](image-url)

Figure 1
can be estimated as $a = 3.845$ Å and $c = 12.19$ Å, indicating that a Na content difference between the two samples is negligible. The dc magnetic susceptibility was measured by using a SQUID magnetometer (MPMS, Quantum Design) under a magnetic field of 5 Oe for the determination of $T_c$.

3. Results and discussion

Figure 1 shows temperature dependence of magnetic susceptibility for S1 isotope samples ($^{54}$Fe and $^{57}$Fe) of (Ca$_{0.4}$Na$_{0.6}$)Fe$_2$As$_2$. The susceptibility is normalized by its value at 5 K. The susceptibility curves exhibit the sharp superconducting transition, indicating our samples are of high quality. Susceptibility curves similar to those are obtained for S2 and S3 isotope samples. No significant difference in the superconducting volume fraction is observed in each combination. The onset $T_c$ is determined from the definition as shown in the inset of Fig. 1. Isotope shifts in $T_c$ are clearly seen, showing that a sample with larger isotope mass has higher $T_c$ in S1. It has been confirmed that a factor for an extrinsic difference in $T_c$ between different isotope samples was ruled out by powder x-ray diffraction measurements. It is considered that the observed isotope shifts in $T_c$ are intrinsic.

Figure 2 shows $T_c$ as a function of the iron isotope mass for different isotope sample sets. Apparently, a sample containing larger isotope mass has higher $T_c$ in each combination. Small differences in $T_c$ between $^{54}$Fe samples as well as $^{57}$Fe samples are presumed to be due to some differences in the Na content $x$, according to our powder x-ray diffraction measurements. Isotope samples synthesized separately must have some differences in the composition, which results in nontrivial changes in $T_c$. This is an issue of isotope sample preparation for iron-based superconductors.

Our results are highly reproducible and evidently demonstrate that $\alpha_{Fe}$ becomes negative. The average of $\alpha_{Fe}$ about all of sample sets is -0.19, which is consistent with $\alpha_{Fe}$ in (Ba$_{0.6}$K$_{0.4}$)Fe$_2$As$_2$ of the same type as (Ca$_{0.4}$Na$_{0.6}$)Fe$_2$As$_2$ [10].

Figure 3 shows $\alpha_{Fe}$ values as a function of $T_c$ obtained in various measurements [10-14]. There is a remarkable difference in $\alpha_{Fe}$ between samples of the same type: FeSe$_{0.35}$Te$_{0.65}$ and FeSe$_{1-x}$. It is hard to explain why the $\alpha_{Fe}$ values show such a large difference if both values are intrinsic. We focus on negative values of $\alpha_{Fe}$ obtained by Shirage et al. [10, 11] and Tsuge et al. [12], since isotope samples which were prepared carefully to rule out any compositional difference were used in their measurements. Apparently, $\alpha_{Fe}$ decreases with decreasing $T_c$, which means that $T_c$ in low-$T_c$ iron-based superconductors is more isotope mass dependent than in high-$T_c$ ones. Although several factors including anharmonic phonons, a pair breaking effect, and van Hove singularity of the density of states may be speculated as the reason why $\alpha_{Fe}$ becomes negative, we notice a factor other than these: a two-band multi-channel effect [15]. Yanagisawa and co-workers [15] calculate negative $\alpha_{Fe}$ values, using a two-band model where electron-phonon interactions and antiferromagnetic spin fluctuations in each band as well as the interband interactions are included. In the model, electron-phonon interactions affect $T_c$; $T_c$ decreases and the negative contribution to $\alpha_{Fe}$ increases as the
intraband electron-phonon interactions become weaker. Actually, band structure calculations [16] show that electron-phonon interactions in the FeSe system are weaker than in the LaFeAsO system. Thus, it is likely that the isotope mass dependence of $T_c$ can be explained by the two-band model.

In conclusion, an iron isotope effect has been observed in (Ca$_{0.4}$Na$_{0.6}$)Fe$_2$As$_2$ in which the Na content is well-controlled. The iron isotope coefficient is estimated to be -0.19, which is consistent with a value [10] observed in (Ba$_{0.6}$K$_{0.4}$)Fe$_2$As$_2$. Definitely, $\alpha_{Fe}$ becomes negative and decreases with decreasing $T_c$ in iron-based superconductors. It seems like that this behaviour originates from two-band superconductivity in which the electron-coupling is mediated by the multi-channel interaction in each band.

References

[1] Kamihara Y et al. 2008 J. Am. Chem. Soc. 130 3296.
[2] Wang C et al. 2008 Europhys. Lett. 83 67006.
[3] Boeri L et al. 2008 Phys. Rev. Lett. 101 026403.
[4] Christianson A D et al. 2008 Nature 456 930.
[5] Imai T et al. 2009 Phys. Rev. Lett. 102 177005.
[6] Hashimoto K et al. 2009 Phys. Rev. Lett. 102 017002.
[7]Evtushinsky D V et al. 2009 New J. Phys. 11 055069.
[8] Nakayama K et al. 2009 EuroPhys.Lett 85 67002.
[9] Bud’ko S L et al. 2001 Phys. Rev. Lett. 86 1877.
[10] Shirage P M et al. 2009 Phys. Rev. Lett. 103 257003.
[11] Shirage P M et al. 2010 Phys. Rev. Lett. 105 037004.
[12] Tsuge Y et al. 2012 Physics Procedia 36 731.
[13] Liu R H et al. 2009 Nature 459 64.
[14] Khasanov R et al. 2010 New J. Phys. 12 073024.
[15] Yanagisawa T et al. 2009 J. Phys. Soc. Jpn. 78 094718.
[16] Boeri L et al. 2009 Physica C 469 628.