

## Absence of an Appreciable Iron Isotope Effect on the Transition Temperature of the Optimally Doped $\text{SmFeAsO}_{1-y}$ Superconductor

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We report the iron (Fe) isotope effect on the transition temperature ( $T_c$ ) in oxygen-deficient  $\text{SmFeAsO}_{1-y}$ , a 50-K-class, Fe-based superconductor. For the optimally doped samples with  $T_c = 54$  K, a change of the average atomic mass of Fe ( $M_{\text{Fe}}$ ) causes a negligibly small shift in  $T_c$ , with the Fe isotope coefficient ( $\alpha_{\text{Fe}}$ ) as small as  $-0.024 \pm 0.015$  (where  $\alpha_{\text{Fe}} = -d \ln T_c / d \ln M_{\text{Fe}}$ ). This result contrasts with the finite, inverse isotope shift observed in optimally doped  $(\text{Ba}, \text{K})\text{Fe}_2\text{As}_2$ , indicating that the contribution of the electron-phonon interaction markedly differs between these two Fe-based high- $T_c$  superconductors.

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High transition temperatures ( $T_c$ ) exceeding 50 K, realized in Fe-based superconductors, have generated worldwide extensive investigations towards discovering new materials with related structures, as well as towards elucidating their superconducting mechanisms. With respect to the latter, the immediate question to be addressed is whether one can understand the high- $T_c$  superconductivity within the conventional framework, namely, the pairing of electrons mediated by the electron-phonon interaction. Otherwise, a more exotic mechanism should be introduced to account for the high- $T_c$  superconductivity.

It is well known that the isotope effect on  $T_c$  has played a crucial role in establishing the basic concept of phonon-mediated superconductivity. In the framework of Bardeen-Cooper-Schrieffer's (BCS) theory, the isotope effect coefficient  $\alpha$ , defined by the relation  $\alpha = -d \ln T_c / d \ln M$ , is equal to 0.5 (in the case of compound superconductors, the sum of all isotope coefficients for the individual elements,  $\alpha = \sum \alpha_i$ , where  $\alpha_i = -d \ln T_c / d \ln M_i$ , becomes 0.5), which is indeed observed in many "conventional" superconductors, such as elemental or binary alloy superconductors [1]. One example of such cases is  $\text{MgB}_2$ , a 38 K high- $T_c$  superconductor in which boron (B) isotope exchange changes its  $T_c$  by 1 K, corresponding to  $\alpha_B = 0.26(3)$ . The result clearly demonstrates that the superconductivity in  $\text{MgB}_2$  is indeed mediated by the electron-phonon interaction [2]. On the other hand, in optimally doped cuprate superconductors, the lack of the oxygen isotope effect [3] has led researchers to search for non-phonon-mediated mechanisms as a source of high- $T_c$  superconductivity. (It should be noted that the lack of the isotope effect itself does not necessarily imply non-phonon-mediated superconductivity. Indeed, several transition element superconductors like Ru and Os show zero isotope coefficients, which are explained by strong electron-phonon coupling [4]).

In the Fe-based superconductors, the essential structural unit is the Fe-As plane. Accordingly, isotope experiments on the Fe or As site should provide crucial information to sort out the role of the electron-phonon interaction in these systems. Based on this motivation, Fe isotope experiments were carried out by two groups. (Since As has only one stable isotope, the As isotope experiment is practically impossible.) Both results indicated the finite isotope shift in  $T_c$ , although they contradict each other. Liu *et al.* carried out  $^{54}\text{Fe}$  isotope exchange on  $\text{SmFeAs}(\text{O},\text{F})$  ( $T_c \sim 42$  K) and  $(\text{Ba}, \text{K})\text{Fe}_2\text{As}_2$  ( $T_c \sim 38$  K), and reported large isotope coefficients  $\alpha_{\text{Fe}} = 0.34$  and  $0.37$ , respectively, which are comparable with the values expected from BCS theory [5]. On the other hand, Shirage *et al.* carried out  $^{54}\text{Fe}$  and  $^{57}\text{Fe}$  isotope exchange on optimally doped  $(\text{Ba}, \text{K})\text{Fe}_2\text{As}_2$  ( $T_c \sim 38$  K) and reported that heavier Fe isotope substitution results in increasing  $T_c$ , yielding the negative  $\alpha_{\text{Fe}} = -0.18(3)$ , referred to as the "inverse" isotope effect [6]. The reason for the discrepancy is yet unclear. It may suggest that the isotope effect significantly depends on the subtle difference among the samples, such as carrier concentration, synthesis technique, lattice strain, etc.

In any case, results on the 40-K-class Fe-based superconductors indicate finite  $\alpha_{\text{Fe}}$ , strongly suggesting that the electron-phonon interaction exists and plays either a positive [5] or a negative [6] role. The natural question to be addressed is whether the Fe isotope shift on  $T_c$  also occurs in other Fe-based superconductors, in particular, those with higher  $T_c$ 's. It is worth recalling that in the case of cuprates, the oxygen isotope effect is negligibly small in the optimally doped samples, while a sizable isotope shift is observed for the under- or over-doped samples, as well as for the lower- $T_c$  materials [7–9]. There is also a possibility that  $\alpha_{\text{Fe}}$  of the Fe-based superconductors exhibits significant material and doping dependence. Along this line of reasoning, in this study we have examined the

Fe isotope effect on a 50-K-class  $\text{SmFeAsO}_{1-y}$  superconductor.

In order to evaluate the Fe isotope effect, one has to prepare the twin samples with different Fe isotopic mass under exactly the same conditions and then precisely compare their  $T_c$ 's. It is technically challenging since the shift in  $T_c$  is estimated to be as small as 1.4 K, even if we assume the full isotope effect ( $\alpha_{\text{Fe}} \sim 0.5$ ) when we substitute heavier  $^{57}\text{Fe}$  with lighter  $^{54}\text{Fe}$ . Moreover,  $T_c$ 's of the  $\text{LnFeAsO}$ -based system strongly depend on their carrier concentration, which is changed by the amount of fluorine substitutions ( $x$ ) in the case of  $\text{LnFeAsO}_{1-x}\text{F}_x$ , or by the amount of oxygen deficiencies ( $y$ ) for  $\text{LnFeAsO}_{1-y}$ . It is critically important that the carrier concentrations of the twin samples are exactly the same and optimally doped. In this regard, before carrying out the isotope exchange experiments, it is necessary to establish the relationship between  $y$  and  $T_c$ , and to find out the optimal carrier concentrations.

In this study, polycrystalline samples of oxygen-deficient  $\text{SmFeAsO}_{1-y}$  were prepared by a high-pressure synthesis method [10,11]. The starting materials were  $\text{Fe}$ ,  $^{54}\text{Fe}_2\text{O}_3$ ,  $^{57}\text{Fe}_2\text{O}_3$ ,  $\text{As}$ ,  $\text{Sm}(\text{OH})_3$ , and a precursor of  $\text{SmAs}$ . For the isotope substitution, we employed  $^{57}\text{Fe}_2\text{O}_3$  and  $^{54}\text{Fe}_2\text{O}_3$  powders, which were obtained by fully oxidizing the  $^{57}\text{Fe}$  enriched powder (ISOFLEX USA, enrichment 95.36%,  $M_{\text{Fe}} = 56.94$ , Fe purity 99.99%) and the  $^{54}\text{Fe}$  enriched powder (ISOFLEX USA, enrichment 99.86%,  $M_{\text{Fe}} = 53.94$ , Fe purity 99.99%), respectively. See supplementary material [12].

As a source of Fe, we used  $^{\text{n}}\text{Fe}$  (natural abundance,  $M_{\text{Fe}} = 55.85$ ) powder instead of using the raw (as-purchased)  $^{57}\text{Fe}$  and  $^{54}\text{Fe}$  metal powders, because the powders were partially oxidized from the beginning and the degree of oxidization was different from powder to powder. Even small oxidation of the starting elements increases the oxygen content  $y$  in the synthesized materials, resulting in the shift of  $T_c$  not due to the isotope exchange but due to the change in carrier concentration.

The materials of  $^{\text{n}}\text{Fe}$ ,  $\text{As}$ ,  $\text{Sm}(\text{OH})_3$ , and  $\text{SmAs}$  were mixed and ground well using an agate mortar, and then divided into two equal parts. Then, the powder was mixed with the  $^{57}\text{Fe}_2\text{O}_3$  (or  $^{54}\text{Fe}_2\text{O}_3$ ) powders and ground again, then pressed into a pellet. These processes were carried out inside a glove box filled with dried  $\text{N}_2$  gas. The two pellets were placed in a BN (see Fig. 2) crucible and heated at about  $1100^\circ\text{C}$  under a pressure of about 3.5 GPa for 2 h. Powder x-ray diffraction (XRD) patterns of the samples were measured using  $\text{CuK}\alpha$  radiation. The dc magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design Magnetic Property Measurement System) under a nominal magnetic field of 5 Oe. The resistivity of the twin samples was measured simultaneously by a four-probe method using Quantum Design Physical Property Measurement System.

Introduction of the oxygen deficiency  $y$  in  $\text{LnFeAsO}_{1-y}$  is reflected as the contraction of the  $a$ - and  $c$ -axis lattice

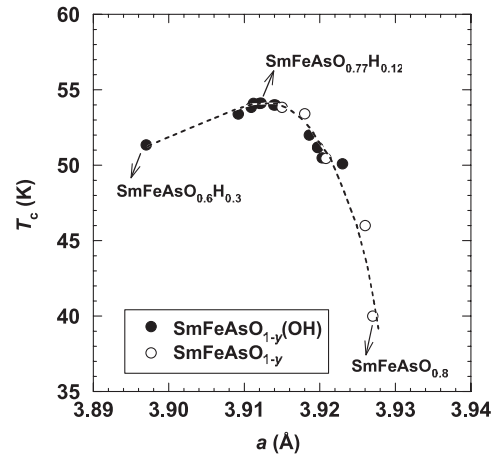


FIG. 1. Dependence of  $T_c$  on the lattice parameter  $a$  in oxygen-deficient  $\text{SmFeAsO}_{1-y}$  and hydroxide added  $\text{SmFeAsO}_{1-y}(\text{OH})_x$ .

parameters [13]. In Ref. [14], we reported that the addition of rare-earth hydroxide to the starting composition causes further contraction of the lattice parameters. Figure 1 represents the  $a$ -parameter dependence of  $T_c$  in  $\text{SmFeAsO}_{1-y}$  and hydroxide added  $\text{SmFeAsO}_{1-y}(\text{OH})_x$ . It shows that  $T_c$  changes quite sensitively with the  $a$  parameter. For the most under-doped samples with a long  $a$ -axis length of  $3.928 \text{ \AA}$ ,  $T_c$  is as low as 40 K. By introducing oxygen deficiency  $y$ ,  $T_c$  increases monotonously up to 54 K, where the  $a$  parameter becomes  $3.915 \text{ \AA}$ , the minimum length that we can reach. Then, by introducing  $\text{Sm}(\text{OH})_3$ , an additional decrease in the  $a$  parameter is realized. Resultantly, a broad, flat-topped peak in  $T_c$  ( $\sim 54 \text{ K}$ ) shows up at around

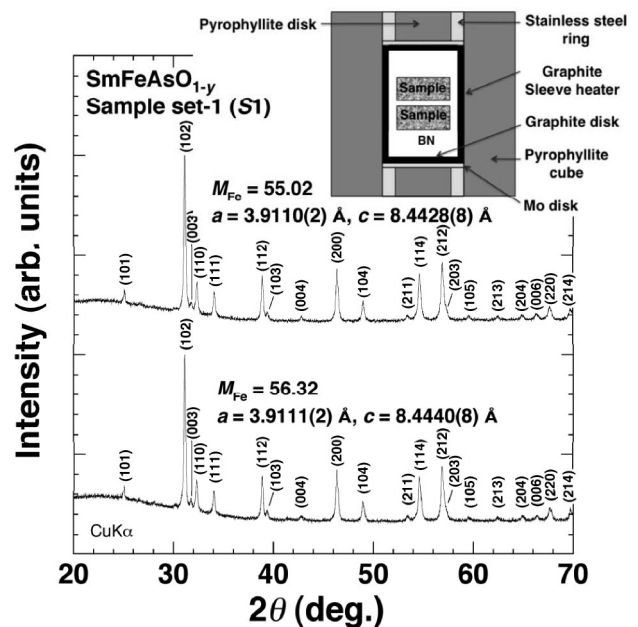


FIG. 2. X-ray diffraction patterns of the sample set S1 synthesized simultaneously under high pressure. The inset shows the sample cell assembly for the high-pressure synthesis method.

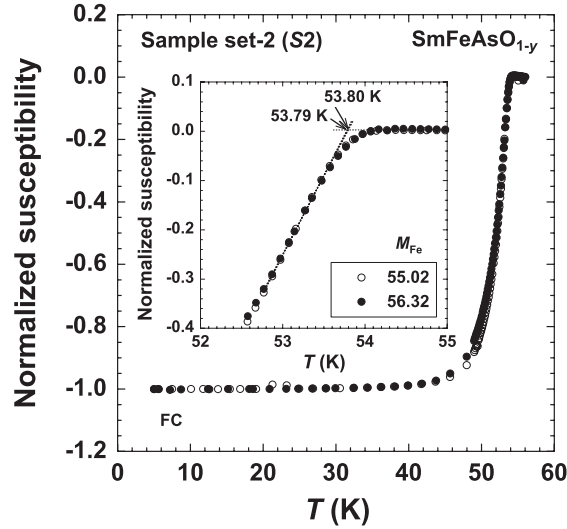


FIG. 3.  $T$  dependence of the FC  $\chi$  for sample set S2 normalized at 5 K and 56 K. The inset shows the  $T$  dependence of  $\chi$  near  $T_c$ . The Fe isotope coefficient is estimated to be  $-0.01$ .

$a = 3.913 \text{ \AA}$ . The existence of the peak in  $T_c$  implies that there is an “optimal” carrier concentration in this system. The existence of this flat-top peak in  $T_c$  allows us to extract the subtle change in  $T_c$  caused by the isotope exchange since the change in  $T_c$  due to the fluctuation of the carrier concentration is minimal around this broad peak.

Having established the ideal synthesis conditions for the isotope experiments, we synthesized the two samples with different Fe isotopes under exactly the same conditions. The nominal composition of the sample is  $\text{SmFeAsO}_{0.77}\text{H}_{0.12}$ , and 43% of Fe in the samples is exchanged by the  $^{57}\text{Fe}$  or  $^{54}\text{Fe}$  isotopes. The resultant  $M_{\text{Fe}}$  are 56.32 and 55.02 for the samples synthesized using the  $^{57}\text{Fe}_2\text{O}_3$  and  $^{54}\text{Fe}_2\text{O}_3$  powders, respectively.

XRD patterns show that the synthesized samples are single phases within the experimental uncertainty, and the lattice parameters of the two samples synthesized at the same time are identical to each other. Figure 2 shows the XRD patterns of the sample set (S1) as a typical example. The  $a$  and  $c$  lattice parameters for the samples with the  $M_{\text{Fe}}$  of 56.32 and 55.02 are  $3.9110(2) \text{ \AA}$ ,  $8.4428(8) \text{ \AA}$  and  $3.9111(2) \text{ \AA}$ ,  $8.4440(8) \text{ \AA}$ , respectively. The  $a$  parameters of both samples correspond to the lattice spacing at which  $T_c$  shows the maximum value in Fig. 1.

Figure 3 represents the temperature ( $T$ ) dependence of the field-cooled (FC) magnetic susceptibility ( $\chi$ ) for the sample set S2. The magnitudes of  $\chi$  at 5 K are around  $-0.01 \text{ emu/g}$ , corresponding to the superconducting volume fraction of 100% without demagnetizing the field correction. In Fig. 3, the magnitude of  $\chi$  is normalized at the 5 K ( $-1$ ) and 56 K ( $0$ ) values for the sake of exact comparison. A sharp superconducting transition allows us to define the accurate  $T_c$  value, as indicated in the inset of Fig. 3. The shift in  $T_c$  for the sample set S2 is at most  $-0.01 \text{ K}$ , which corresponds to  $\alpha_{\text{Fe}} = -0.01$ .

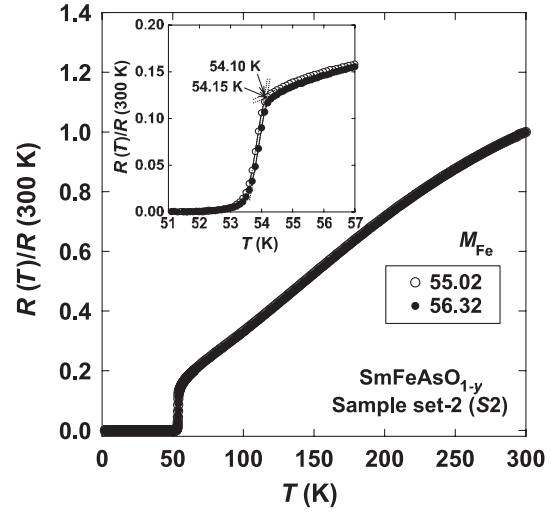


FIG. 4.  $T$  dependence of resistivity  $\rho$  (normalized at 300 K) of the sample set S2. The inset shows the  $T$  dependence of  $\rho$  near  $T_c$ . The Fe isotope coefficient is estimated to be  $-0.04$ .

Figure 4 shows  $T$ -dependent resistivity ( $\rho$ ) of the sample set S2. Here again, the magnitude of  $\rho$  is normalized using the 300 K value. The  $\rho$  data almost overlap with each other, indicative of the same carrier concentrations of the two samples. The  $T_c$ 's of the samples are determined by the onset of the resistive transition, and are 54.15 K and 54.10 K for  $M_{\text{Fe}} = 56.32$  and 55.02, respectively, as shown in the inset of Fig. 4. The estimated  $\alpha_{\text{Fe}}$  is  $-0.04$ , which is comparable with that obtained from  $\chi$ .

Table I summarizes the  $M_{\text{Fe}}$  dependence of  $T_c$  determined from  $\chi$  for five sample sets, S1–S5. The absolute value of  $T_c$  is highly reproducible ( $54.02 \text{ K} \pm 0.13 \text{ K}$ ), and the difference in  $T_c$  caused by the isotope substitution is at most  $-0.05 \text{ K}$ , yielding an average  $\alpha_{\text{Fe}}$  of  $-0.024 \pm 0.015$ . If we assume  $\alpha_{\text{Fe}}$  as 0.5, the isotope shift is expected to be  $0.60 \text{ K}$ , which is 1 order of magnitude larger than the value obtained from the experiments. The results presented here evidently demonstrate that  $\alpha_{\text{Fe}}$  is very small in the optimally doped, highest- $T_c$   $\text{SmFeAsO}_{1-y}$  samples.

TABLE I. The Fe average atomic mass ( $M_{\text{Fe}}$ ) dependence of the  $T_c$  determined from  $\chi$  for five sample sets, S1–S5.

Sample sets	$M_{\text{Fe}}$	$T_{c(\chi)}$ (K)	$\Delta T_{c(\chi)}$ (K)	$\alpha_{\text{Fe}}$
S1	55.02	54.02	-0.05	-0.040
	56.32	54.07		
S2	55.02	53.79	-0.01	-0.008
	56.32	53.80		
S3	55.02	53.96	-0.02	-0.016
	56.32	53.98		
S4	55.05	54.10	-0.02	-0.016
	56.31	54.12		
S5	55.02	54.13	-0.05	-0.040
	56.32	54.18		
Average $\alpha_{\text{Fe}}$				$-0.024 \pm 0.015$

TABLE II.  $\lambda_{AF}$  and  $\lambda_{ph}$  deduced from Eqs. (1) and (3) using the observed  $T_c$  and  $\alpha_{Fe}$  values for (Ba, K)Fe<sub>2</sub>As<sub>2</sub> and SmFeAsO<sub>1-y</sub>.

	Observed		Provided		Deduced	
	$T_c$ (K)	$\alpha_{Fe}$	$\omega_{ph}$ (K)	$\lambda_{ph}/\lambda_{AF}^*$	$\lambda_{AF}^*$	$\lambda_{ph}$
(Ba, K)Fe <sub>2</sub> As <sub>2</sub>	38	$-0.18 \pm 0.03$	350	$-0.14 \pm 0.02$	$0.50 \pm 0.01$	$-0.07 \pm 0.01$
SmFeAsO <sub>1-y</sub>	54	$-0.02 \pm 0.01$	350	$-0.02 \pm 0.01$	$0.51 \pm 0.01$	$-0.01 \pm 0.005$

Naively thinking, the negligibly small  $\alpha_{Fe}$  may indicate that the superconductivity in this material is not caused by the electron-phonon interaction. (At this moment, there still exists the possibility that there is a finite isotope effect at the As site.)

Our result is apparently in contradiction with a large  $\alpha_{Fe} = 0.34$  on SmFeAsO<sub>0.85</sub>F<sub>0.15</sub> ( $T_c = 42$  K), as reported by Liu *et al.* [5]. Giving lower  $T_c$ 's of their samples in comparison to the present ones, their samples are probably located at the under-doped region and the apparent difference might arise from the different carrier concentration of the samples. If this is the case, this situation resembles the cuprate superconductors [7–9].

Here we attempt to analyze the  $\alpha_{Fe}$  of SmFeAsO<sub>1-y</sub> and (Ba, K)Fe<sub>2</sub>As<sub>2</sub> by taking into account the possible competition between the contributions from phonons and anti-ferromagnetic (AF) spin fluctuations, as we have presented in a previous paper to explain the inverse isotope effect in (Ba, K)Fe<sub>2</sub>As<sub>2</sub> [6,15]. According to this model,  $T_c$  and  $\alpha$  are described as

$$k_B T_c = 1.13 \omega_{ph} \exp\left(-\frac{1}{\lambda_{ph} + \lambda_{AF}^*}\right), \quad (1)$$

where

$$\lambda_{AF}^* = \frac{\lambda_{AF}}{1 - \lambda_{AF} \ln(\omega_{AF}/\omega_{ph})}, \quad (2)$$

$$\alpha = \frac{1}{2} \left[ 1 - \left( \frac{\lambda_{AF}^*}{\lambda_{ph} + \lambda_{AF}^*} \right)^2 \right], \quad (3)$$

where  $\lambda_{AF}$ ,  $\omega_{AF}$ ,  $\lambda_{ph}$ ,  $\omega_{ph}$  are the dimensionless coupling constants and characteristic energies of the AF spin fluctuation and phonon, respectively.  $\lambda_{ph}$  is defined by  $\lambda_{ph}^{intra} - \lambda_{ph}^{inter}$ , where  $\lambda_{ph}^{intra}$  and  $\lambda_{ph}^{inter}$  are the dimensionless electron-phonon coupling constants for intraband and interband pair hoppings, respectively. In the present calculation we provided [16] the value of  $\omega_{ph} = 350$  K. The  $\lambda_{AF}^*$  and  $\lambda_{ph}$  deduced from Eqs. (1) and (3) by using the observed  $T_c$  and  $\alpha_{Fe}$  values are listed in Table II.

One can see that the values of  $\lambda_{AF}^*$  are almost the same for both systems at their optimal  $T_c$ . Within the present framework, the higher  $T_c$  for SmFeAsO<sub>1-y</sub> in comparison to (Ba, K)Fe<sub>2</sub>As<sub>2</sub> is ascribed to the smaller magnitude of  $\lambda_{ph}$ , namely, the larger (negative) contribution of the intraband electron-phonon coupling, rather than the larger  $\lambda_{AF}^*$ . The lack of the isotope effect in the optimally doped

SmFeAsO<sub>1-y</sub> implies that the  $\lambda_{ph}^{interband}$  is comparable to the  $\lambda_{ph}^{intra}$ . According to this model,  $T_c$  can be enhanced if the intraband electron-phonon interaction works cooperatively with the AF spin fluctuation ( $\lambda_{ph}^{intra} > \lambda_{ph}^{inter}$ ).

In summary, we have studied the Fe isotope effect on  $T_c$  in the optimally doped SmFeAsO<sub>1-y</sub> ( $T_c = 54$  K). A change of the  $M_{Fe}$  yields a negligibly small shift in  $T_c$ , with its  $\alpha_{Fe}$  as small as  $-0.024 \pm 0.015$ . This result indicates that  $\alpha_{Fe}$  strongly depends on the system and carrier concentrations. To clarify the issue, it is desirable to evaluate  $\alpha_{Fe}$  as a function of the doping level for Fe-based systems in the future.

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