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Iron isotope effect on the superconducting transition temperature and the crystal structure of FeSe$_{1-x}$

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Abstract. The Fe isotope effect (Fe-IE) on the transition temperature $T_c$ and the crystal structure was studied in the Fe chalcogenide superconductor FeSe$_{1-x}$ by means of magnetization and neutron powder diffraction (NPD). The substitution of natural Fe (containing $\approx 92\%$ of $^{56}\text{Fe}$) by its lighter $^{54}\text{Fe}$ isotope leads to a shift of $T_c$ of 0.22(5) K corresponding to an Fe-IE exponent of $\alpha_{Fe} = 0.81(15)$. Simultaneously, a small structural change with isotope substitution is observed by NDP which may contribute to the total Fe isotope shift of $T_c$.

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Historically, the isotope effect played a crucial role in elucidating the origin of the pairing interaction leading to the occurrence of superconductivity. The discovery of the isotope effect on the superconducting transition temperature \( T_c \) in Hg \([1]\) in 1950 provided the key experimental evidence for phonon-mediated pairing as formulated theoretically by BCS subsequently. The observation of unusually high \( T_c \)'s in the newly discovered Fe-based superconductors immediately raised the question regarding the pairing glue and initiated isotope effect studies. Currently, we are aware of two papers on isotope experiments with, however, contradicting results. Liu et al. \([2]\) showed that in SmFeAsO\(_{0.85}\)F\(_{0.15}\) and Ba\(_{0.6}\)K\(_{0.4}\)Fe\(_2\)As\(_2\) the Fe isotope effect (Fe-IE) exponent,

\[
\alpha_{\text{Fe}} = -d \ln T_c/d \ln M_{\text{Fe}} = -(\Delta T_c/T_c)/(\Delta M_{\text{Fe}}/M_{\text{Fe}}),
\]

(reaches values of \( \alpha_{\text{Fe}} \simeq 0.35 \) (\( M_{\text{Fe}} \) is the Fe atomic mass), while Shirage et al. \([3]\) found a negative Fe-IE exponent \( \alpha_{\text{Fe}} \simeq -0.18 \) in Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\). Note, that the only difference between the Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) samples studied in Refs. \([2]\) and \([3]\) was the preparation procedure (low-pressure synthesis in \([2]\) vs. high-pressure synthesis in \([3]\)), while the potassium doping (\( x \simeq 0.4 \)) as well as the \( T_c \)'s for the samples containing natural Fe (\( T_c \simeq 37.3 \) K in \([2]\) vs. \( T_c \simeq 37.8 \) K in \([3]\)) were almost the same.

In this paper we study the Fe-IE on \( T_c \) and on the structural parameters (such as the lattice parameters \( a, b, \) and \( c \), the lattice volume \( V \), and the distance between the Se atom and Fe plane, Se height \( h_{\text{Se}} \)) for another representative of the Fe-based high-temperature superconductors (HTS), namely FeSe\(_{1-x}\). The substitution of natural Fe (containing \( \simeq 92\% \) of \(^{56}\text{Fe}\)) by its lighter \(^{54}\text{Fe}\) isotope leads to a shift of \( T_c \) of 0.22(5) K corresponding to an Fe-IE exponent of \( \alpha_{\text{Fe}} = 0.81(15) \).

The \(^{54}\text{FeSe}_{1-x}/^{56}\text{FeSe}_{1-x}\) samples (here after we denote natural Fe containing \( \simeq 92\% \) of \(^{56}\text{Fe}\) isotope as \(^{56}\text{Fe}\)) with the nominal composition FeSe\(_{0.98}\) were prepared by a solid state reaction made in two steps. Pieces of Fe (natural Fe: 99.97% minimum purity, average atomic mass \( M_{\text{Fe}} = 55.85 \) g/mol, or \(^{54}\text{Fe}: 99.99\% \) purity, 99.84% isotope enriched, \( M_{^{54}\text{Fe}} = 54.0 \) g/mol) and Se (99.999% purity) were first sealed in double walled quartz ampules, heated up to 1075°C, annealed for 72 h at this temperature and 48 h at 420°C, and then cooled down to room temperature at a rate of 100°C/h. As a next step, the samples, taken out of the ampules, were powderised, pressed into pellets, sealed into new ampules and annealed first at 700°C for 48 h and then at 400°C for 36 h, followed by cooling to room temperature at a rate of 200°C/h. Due to the extreme sensitivity of FeSe\(_{1-x}\) to oxygen \([4]\), all the intermediate steps (grinding and pelletizing) as well as the preparation of the samples for the neutron powder diffraction and magnetization experiments were performed in a glove box under He atmosphere.

The Fe-IE on the structural properties was studied by neutron powder diffraction (NPD) experiments by using the high-resolution powder diffractometer HRPT (Paul Scherrer Institute, Switzerland) \([5]\). The experiments were carried out at a wavelength \( \lambda = 1.494 \) Å. The \(^{54}\text{FeSe}_{1-x}/^{56}\text{FeSe}_{1-x}\) samples, placed into vanadium containers, were mounted into a He-4 cryostat in order to reach temperatures between 5 and 250 K. High statistics data were taken at 250 and 5 K. Data at \( 10 \leq T \leq 240 \) K were collected with
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intermediate statistics.

**Figure 1.** (Color online) The Rietveld refinement pattern and difference plot of NPD data for $^{54}$FeSe$_{1-x}$ (panel a) $^{56}$FeSe$_{1-x}$ (panel b) at $T = 250$ K. The rows of ticks show the Bragg-peak positions for the main phase FeSe ($P4_{nmm}$) and two impurity phases: Fe ($Im3m$) and hexagonal FeSe ($P6_3/mmc$). The main tetragonal phase corresponds to 0.975(5) and 0.975(4) Se occupancy for $^{54}$FeSe$_{1-x}$ and $^{56}$FeSe$_{1-x}$, respectively.

Figure 1 shows the NPD spectra taken at $T = 250$ K. The differences in peak intensities, clearly visible at small $\theta$, are caused by the different values of the coherent neutron scattering length ($b_{coh}$) of natural Fe and that of the $^{54}$Fe isotope. The refinement of the crystal structure was performed by using the FULLPROF program [6] with $b_{coh}^{Fe} = 9.45 \cdot 10^{-15}$ m, $b_{coh}^{54Fe} = 4.2 \cdot 10^{-15}$ m, and $b_{coh}^{Se} = 7.97 \cdot 10^{-15}$ m [7]. The refined structural parameters at $T = 250$ K and 5 K are summarized in Table 1. The amount of the impurity phases and the Se content ($1-x$), determined for the data sets taken at $T = 250$ K, were kept fixed during the refinement of the NPD spectra at lower temperatures. The mass fractions of impurity phases, the hexagonal FeSe ($P6_3/mmc$) and Fe ($Im3m$), were found to be 0.50(10)$\%$, 0.31(4)$\%$ and 1.13(18)$\%$, 1.06(7)$\%$ for $^{54}$FeSe$_{1-x}$ and $^{56}$FeSe$_{1-x}$, respectively.

Figure 2 shows the temperature dependence of the lattice parameters $a$, $b$, and $c$, the lattice volume $V$, and the Se height $h_{Se}$ of a representative $^{54}$FeSe$_{1-x}$ and a representative $^{56}$FeSe$_{1-x}$ sample (see Fig. 3). From Fig. 2a it is obvious that at $T_s \simeq 100$ K a transition from a tetragonal to an orthorhombic structure takes place, analogous to that reported in [4, 8]. The Fe-IE on the structural transition temperature $T_s$ could be estimated from the shift of the interception point of the linear fits to $a(T)$ and $b(T)$ in the vicinity of $T_s$, as denoted by the arrows in the inset of Fig. 2a, which was found to be $\Delta T_s = 0.2(2.5)$ K. Within the whole temperature range (5 K $\leq T \leq 250$ K) the
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Table 1. Structural parameters of $^{54}$FeSe$_{1-x}$ and $^{56}$FeSe$_{1-x}$ at $T = 250$ and 5 K. Space group $P4/nmm$ (no. 129), origin choice 2: Fe in (2b) position (1/4, 3/4, 1/2); Se in (2c) position (1/4, 1/4, z). Space group $Cmma$ (no. 67): Fe in (4b) position (1/4, 0, 1/2), Se in (4g) position (0, 3/4, z). The atomic displacement parameters ($B$) for Fe and Se were constrained to be the same. The Bragg $R$ factor is given for the main phase; the other reliability factors are given for the whole refinement.

|                | $T = 250$ K                  |                | $T = 5$ K                   |
|----------------|-----------------------------|----------------|-----------------------------|
|                | $^{54}$FeSe$_{1-x}$          | $^{56}$FeSe$_{1-x}$ | $^{54}$FeSe$_{1-x}$          | $^{56}$FeSe$_{1-x}$ |
| Space group    | $P4/nmm$                    | $Cmma$         | fixed to 0.975               |
| Se content     | 0.975(5)                    | 0.975(4)       |                             |
| $a$(Å)         | 3.77036(3)                  | 3.76988(5)     | 5.33523(10)                 | 5.33426(10)     |
| $b$(Å)         | 5.51619(9)                  | 5.51637(9)     | 5.48683(9)                  | 5.48787(9)     |
| $c$(Å)         | 156.883(3)                  | 156.797(3)     | 155.438(5)                  | 155.424(5)     |
| Volume (Å$^3$) | 0.2319(2)                   | 0.2326(0.3)    | 0.2321(2)                   | 0.2322(3)      |
| $B$(Å$^2$)     | 1.02(2)                     | 0.93(2)        | 0.44(2)                     | 0.36(2)        |
| $R_{Bragg}$    | 3.11                        | 2.93           | 4.13                        | 3.63           |
| $R_{wp}$       | 3.93                        | 3.72           | 5.16                        | 4.62           |
| $R_{exp}$      | 3.13                        | 3.05           | 4.73                        | 4.03           |
| $\chi^2$      | 1.58                        | 1.49           | 1.19                        | 1.32           |

Lattice constants $a$ and $b$ are slightly larger for $^{54}$FeSe$_{1-x}$ than those for $^{56}$FeSe$_{1-x}$ (see Fig. 2a). This is in contrast to the lattice parameter $c$, which within the same range is marginally smaller for $^{54}$FeSe$_{1-x}$ than for $^{56}$FeSe$_{1-x}$ (Fig. 2b). The lattice volume remains, however, unchanged. Consequently, substitution of $^{56}$Fe by $^{54}$Fe leads to a small, but detectable enhancement of the lattice along the crystallographic $a$ and $b$ directions and a compression of it along the $c$-axis, resulting in a change of the shape of the Fe$_4$Se pyramid, which is known to influence $T_c$ in Fe-based HTS [9, 10, 11]. This is shown in Fig. 2: where below 100 K the Se atom is located closer to the Fe plane in $^{54}$FeSe$_{1-x}$ than in $^{56}$FeSe$_{1-x}$. The corresponding change of the Fe$_4$Se pyramid is shown schematically in the inset of Fig. 2c. It is important to note that the observed Fe-IE's on the lattice parameters are intrinsic and not just a consequence of slightly different samples. As shown in Ref. [4], various samples of $^{56}$FeSe$_{1-x}$ with $1 - x \simeq 0.98$ and $T_c \simeq 8.2$ K indeed exhibit the same lattice parameters within experimental error.

The Fe-IE on the transition temperature $T_c$ was studied by means of magnetization experiments. Measurements were performed by using a SQUID magnetometer (Quantum Design MPMS-7) in a field of $\mu_0H = 0.1$ mT for temperatures ranging from 2 to 20 K. In order to avoid artifacts and systematic errors in the determination of the isotope shift of $T_c$ it is important to perform a statistical study: i.e. to investigate
values are:

The average calculated for the rest of the six samples. We have no explanation for this discrepancy, but decided to show this point for completeness of the data collected.

The magnetization curve with the small paramagnetic offset $M_{\text{magn}}$ measured at $T > T_c$ further normalization of the obtained curve to the value at $T = 2$ K, see Fig. 1 in Ref. [4] for details). The magnetization curve for $^{54}\text{FeSe}_{1-x}$ is shifted almost parallel to higher temperature, implying that $T_c$ of $^{54}\text{FeSe}_{1-x}$ is higher than that of $^{56}\text{FeSe}_{1-x}$. The resulting transition temperatures determined from the intercept of the linearly extrapolated $M_{\text{norm}}(T)$ curves with the $M = 0$ line for all samples investigated are summarized in Fig. 3. The $T_c$'s for both sets of $^{54}\text{FeSe}_{1-x}/^{56}\text{FeSe}_{1-x}$ samples fall into two distinct regions: $8.39 \leq ^{54}T_c \leq 8.48$ K and $8.15 \leq ^{56}T_c \leq 8.31$ K, respectively. The corresponding mean values are: $^{54}T_c = 8.43(3)$ K and $^{56}T_c = 8.21(4)$ K. Note, that one out of the seven $^{56}\text{FeSe}_{1-x}$ samples had $T_c \approx 8.44$ K which is by more than 5 standard deviations above the average calculated for the rest of the six samples. We have no explanation for this discrepancy, but decided to show this point for completeness of the data collected.

The Fe-IE exponent $\alpha_{\text{Fe}}$ was determined from the data presented in Fig. 3 using Eq. (1), where the relative Fe isotope shift of the quantity $X$ is defined as $\Delta X/X = (^{54}X - ^{56}X)/^{56}X$ (this definition of $\Delta X/X$ is used throughout the paper). With $^{54}T_c = 8.43(3)$ K, $^{56}T_c = 8.21(4)$ K, $M_{54\text{Fe}} = 54$ g/mol, and $M_{56\text{Fe}} = 55.85$ g/mol one obtains $\alpha_{\text{Fe}} = 0.81(15)$. Two points should be emphasized: i) The positive sign of the Fe-IE exponent $\alpha_{\text{Fe}}$ is similar to that observed in phonon mediated superconductors, such as elemental metals [1] and MgB$_2$ [12] as well as in cuprate HTS [13, 14] where the pairing mechanism is still under debate. Bearing in mind that a positive Fe-IE exponent was also observed in SmFeAsO$_{0.88}$F$_{0.15}$ and Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ [2], we may conclude that at least for three compounds representing different families of Fe-based HTS (1111, 122, and 11) the sign of the Fe-IE on $T_c$ is conventional. This suggests that the lattice plays an essential role in the pairing mechanism in the Fe-based HTS. ii) The Fe-IE exponent $\alpha_{\text{Fe}} = 0.81(15)$ is larger than the BCS value $\alpha_{\text{BCS}} = 0.5$ as well as more than twice as large as $\alpha_{\text{Fe}} \approx 0.35$ reported for SmFeAsO$_{0.88}$F$_{0.15}$ and Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ [2]. Note that an enhanced value of the oxygen isotope exponent ($\alpha_{O} \approx 1$) was also observed in underdoped cuprate HTS [14] and was shown to be a consequence of the polaronic nature of the supercarriers in that class of materials [15]. Recently, Bussmann-Holder et al. [16] showed that in the framework of a two-band model polaronic coupling in the larger gap channel as well as in the interband interaction induce a $T_c$ (doping) dependent Fe-IE: $\alpha_{\text{Fe}}$ increases strongly with reduced $T_c$ (doping), reaching $\alpha_{\text{Fe}} \approx 0.9$ at $T_c \approx 10$ K. Note that a similar generic trend is observed in cuprate HTS [13, 14].

However, our structural refined NPD data suggest that part of the large Fe-IE $\alpha_{\text{Fe}} = 0.81(15)$ may result from the tiny structural changes due to $^{54}\text{Fe}/^{56}\text{Fe}$ substitution. In the following we discuss a possible structural effect on the observed Fe-IE on $T_c$. It is known that in $\text{FeSe}_{1-x}$ a decrease of the Se height caused by compression of the

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Fe$_4$Se pyramid leads to an increase of $T_c$ by $\Delta T_{c}^{\text{hSe}}/(\Delta h_{\text{Se}}/h_{\text{Se}}) \approx 3.4$ K/% \cite{11, 17}. In contrast, an increase of the Se(Fe)-Fe-Se(Fe) angle in the FeSe$_{1-y}$Te$_y$ family (angle $\beta$ in our notation \cite{18}, see the inset of Fig. 2c) results for $y \leq 0.5$ in a decrease of $T_c$ by $\Delta T_{c}^{\beta}/(\Delta \beta/\beta) \approx 2.9$ K/% \cite{10}. Based on the structural data presented in Fig. 2 one obtains $\Delta h_{\text{Se}}/h_{\text{Se}} = 0.22(8)\%$ and $\Delta \beta/\beta = -0.13(4)\%$, leading to $\Delta T_{c}^{\text{hSe}} = 0.7(3)$ K and $\Delta T_{c}^{\beta} = -0.4(2)$ K (in this estimate the values of the lattice constants $a$ and $b$, and $h_{\text{Se}}$ were averaged over the temperature regions denoted as solid lines in Figs. 2a and c). Bearing in mind that all Fe-based HTS are similarly sensitive to structural changes as FeSe$_{1-x}$ (see, e.g., \cite{9, 10, 11, 19}) we conclude that the shift of $T_c$ caused by tiny modifications of the crystal structure upon isotope exchange may contribute to the total Fe-IE exponent. However, the large errors of $\Delta T_{c}^{\text{hSe}}$ and $\Delta T_{c}^{\beta}$ do not allow a reliable estimate of this structural effect on the Fe-IE on $T_c$. A better estimate of this effect can be made based on the empirical relation between $T_c$ and the lattice parameter $a$ for the 11 family FeSe$_{1-y}$Te$_y$ \cite{10, 19}. Assuming that the relation $T_c(a)$ is also valid for FeSe$_{1-x}$ one obtains from the data presented in Ref. \cite{19} for $y \leq 0.5$ the relation $\Delta T_{c}^{a}/(\Delta a/a) \approx 6$ K/%. With $(\Delta a + \Delta b)/(a + b) = 0.0195(14)\%$ this gives rise to a structural shift of $T_c$ of $\Delta T_{c}^{\text{str}} \approx 0.1$ K (the lattice constants $a$ and $b$ were averaged over the temperature regions marked as solid line in Fig. 2h). Taking this correction into account yields a rough estimate of the intrinsic Fe-IE exponent of $\alpha_{\text{Fe}}^{\text{int}} \approx 0.4$. This value is comparable with $\alpha_{\text{Fe}} \approx 0.35$ reported for SmFeAsO$_{0.85}$F$_{0.15}$ and Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ \cite{2}.

To summarize, the $^{56}$Fe/$^{54}$Fe isotope effects on the superconducting transition temperature and the crystal structure were studied in the iron chalcogenide superconductor FeSe$_{1-x}$. The following results were obtained: (i) The substitution of the natural Fe ($M_{\text{Fe}} = 55.85$ g/mol) by the $^{54}$Fe isotope ($M_{\text{Fe}} = 54.0$ g/mol) gives rise to a pronounced Fe isotope shift of the transitions temperature $T_c$ as determined by magnetization measurements. The average $T_c$ is found to be $\approx 0.22$ K higher for the $^{54}$FeSe$_{1-x}$ samples as compared to the $^{56}$FeSe$_{1-x}$ samples resulting in a Fe-IE exponent of $\alpha_{\text{Fe}} = 0.81(15)$. (ii) The $^{56}$Fe/$^{54}$Fe isotope substitution leads to an enhancement of the lattice constants $a$ and $b$ and a shrinkage of the lattice constant $c$. These modifications do not affect the lattice volume. (iii) The tetragonal to orthorhombic structural transition temperature ($T_s \approx 100$ K) is the same for both $^{54}$FeSe$_{1-x}$ and $^{56}$FeSe$_{1-x}$ within the accuracy of the experiment. (iv) For temperatures below 100 K the distance between the Se atom and Fe plane (Se height) is smaller for the samples with $^{54}$Fe. This, together with the results of point ii), imply that $^{56}$Fe/$^{54}$Fe isotope substitution leads to a compression of the Fe$_4$Se pyramid along the crystallographic $c-$axis and an enhancement along the $a-$ and $b-$directions. (v) The structural changes caused by $^{56}$Fe/$^{54}$Fe isotope substitution induce a shift in $T_c$ which may reduce the value of Fe-IE exponent to $\approx 0.4$, in fair agreement with $\alpha_{\text{Fe}} \approx 0.35$ obtained for SmFeAsO$_{0.85}$F$_{0.15}$ and Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ \cite{2}.

In conclusion, from magnetization experiments the Fe-IE exponent of $T_c$ for the FeSe$_{1-x}$ system was determined to be $\alpha_{\text{Fe}} = 0.81(15)$. The tiny changes of the structural parameters caused by isotope substitution may contribute to the total Fe-IE exponent,
Iron isotope effect on $T_c$ and the crystal structure of FeSe$_{1-x}$ and may help to clarify or even be the origin of the previously reported controversial results [2, 3]. However, more detailed and systematic structural investigations on Fe isotope substituted samples are required in order to draw definite conclusions. Our findings, on the other hand, clearly show that a conventional isotope effect on $T_c$ is present which highlights the role of the lattice in the pairing mechanism in this new material class.

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Figure 2. (Color online) The temperature dependence of the lattice constants $a$ and $b$ (panel a, in the tetragonal phase $a$ is multiplied by $\sqrt{2}$), lattice constant $c$ (panel b), and the distance between the Se atom and Fe plane $h_{\text{Se}}$ (panel c) for $^{54}\text{FeSe}_{0.975(5)}$ and $^{56}\text{FeSe}_{0.975(4)}$ samples. The inset in panel a shows the extended part of $a(T)$ and $b(T)$ in the vicinity of the structural transition temperature $T_s$, together with the linear fits. The inset in panel b represents the temperature dependence of the lattice volume $V$. The inset in panel c shows schematically the modification of the Fe$_4$Se pyramid caused by $^{56}\text{Fe}/^{54}\text{Fe}$ isotope substitution. The arrows show the direction of atom displacements (see text for details).
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Figure 3. (Color online) The superconducting transition temperature $T_c$ as a function of Fe atomic mass for $^{54}$FeSe$_{1-x}$/56FeSe$_{1-x}$ samples studied in the present work. The open symbols correspond to the samples studied by NPD experiments. The $T_c$’s fall into the regions marked by the colored stripes with the corresponding mean values $^{54}T_c = 8.43(3)$ K and $^{56}T_c = 8.21(4)$ K. The inset shows the normalized ZFC magnetization curves $M_{norm}(T)$ for one pair of $^{54}$FeSe$_{1-x}$ and $^{56}$FeSe$_{1-x}$ samples. The transition temperature $T_c$ is determined as the intersection of the linearly extrapolated $M_{norm}(T)$ curve in the vicinity of $T_c$ with the $M = 0$ line.