Isotope effect on the transition temperature $T_c$ in Fe-based superconductors: the current status

Rustem Khasanov\textsuperscript{1}

\textsuperscript{1}Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

The results of the Fe isotope effect (Fe-IE) on the transition temperature $T_c$ obtained up to date in various Fe-based high temperature superconductors are summarized and reanalyzed by following the approach developed in [Phys. Rev. B \textbf{82}, 212505 (2010)]. It is demonstrated that the very controversial results for Fe-IE on $T_c$ are caused by small structural changes occurring simultaneously with the Fe isotope exchange. The Fe-IE exponent on $T_c$ $\alpha_{Tc} = -(\Delta T_c/T_c)/(\Delta M/M)$, $M$ is the isotope mass needs to be decomposed into two components with the one related to the structural changes ($\alpha_{Tc}^{\text{str}}$) and the genuine (intrinsc one, $\alpha_{Tc}^{\text{int}}$). The validity of such decomposition is further confirmed by the fact that $\alpha_{Tc}^{\text{int}}$ coincides with the Fe-IE exponent on the characteristic phonon frequencies $\alpha_{ph}^{\text{int}}$ as is reported in recent EXAFS and Raman experiments.

I. INTRODUCTION

Historically, the isotope effect plays an important 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 metallic Hg\textsubscript{122} in the year 1950 provided the key experimental evidence for phonon-mediated pairing and leads to the subsequent formulation of the BCS theory. An involvement of the lattice degrees of freedom into the supercarrier formation is generally considered by measuring the isotope effect exponent on $T_c$:

$$\alpha = -\frac{\Delta T_c/T_c}{\Delta M/M}, \quad (1)$$

($M$ is the isotope mass and $\Delta M$ is the mass difference) and by further comparing it with the universal value $\alpha_{BCS} = 0.5$ as is predicted within the framework of BCS theory of electron-phonon mediated superconductivity.

In conventional phonon-mediated superconductors like simple metals, alloys, etc., $\alpha$, typically, ranges from 0.2 to 0.5, (see Ref. 3 and references therein). The only exceptions are Ru and Zr exhibiting zero isotope effect and PdH(D) with $\alpha_{H(D)} = -0.25$\textsuperscript{4,5}. The negative isotope effect of PdH(D) is explained, however, by the presence of strong lattice anharmonicity caused by the double-well potential in the proton (deuteron) bond distribution\textsuperscript{2}. A similar finding exists in organic superconductors where the H(D) isotope effect changes sign as compared, e.g., to $^{34}\text{S}, ^{13}\text{C}$, and $^{15}\text{N}$ isotope replacements, (see Ref. 7 and references therein). Again, an unusually strong anharmonic lattice dynamics are attributed to this observation\textsuperscript{7,8}. Recently the sín changed isotope effect was reported by Stucky et al.\textsuperscript{2} for n-doped SrTiO\textsubscript{3} which supposed to be purely phonon-mediated superconductor. It was observed that the substitution of the natural $^{16}\text{O}$ atoms by the heavier isotope $^{18}\text{O}$ causes a giant (of the order of 50\%) enhancement of $T_c$. Also the magnetic critical field $H_{c2}$ is increased by a factor $\sim 2$. Such a strong impact on $T_c$ and $H_{c2}$, with a sign opposite to conventional superconductors was assumed to be caused by strong coupling to the ferroelectric soft modes of SrTiO\textsubscript{3}.

The cuprate high-temperature superconductors (HTS) are characterized by a vanishingly small but positive isotope effect exponent in optimally doped compounds which increases in a monotonic way upon decreasing doping\textsuperscript{41–43}. For the optimally doped cuprate HTS the smallest value of the oxygen-isotope exponent $\alpha_O \approx 0.02$ was obtained for YBa$_2$Cu$_3$O$_{7-\delta}$ and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$, while it reaches $\alpha_O \approx 0.25$ for Bi$_2$Sr$_2$La$_{0.4}$CuO$_{6+\delta}$.\textsuperscript{10–13,23,24} In addition, it was demonstrated that in underdoped materials $\alpha_O$ exceeds substantially the BCS limit $\alpha_{BCS} \equiv 0.5$\textsuperscript{13,24}.

It is worth to emphasize here that the values of both, the oxygen and the copper isotope exponents in cuprate HTS are always positive. Similar tendencies, with the only few above mentioned exceptions, are also realized in a case of conventional phonon-mediated superconductors.

Since the discovery of high-temperature superconductivity in Fe-based compounds few experiments to study the isotope effect on $T_c$ in this new class of materials were performed. The current statement of isotope effect on Fe-based HTS remains, however, rather controversial. The Fe-IE exponent $\alpha_{Fe}$ for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ ($T_c \approx 38$ K), SmFeAsO$_{0.85}$Fe$_{0.15}$ ($T_c \approx 41$ K), and FeSe$_{1-x}$ ($T_c \approx 8$ K) with the corresponding values $\alpha_{Fe} = 0.34(3)$, 0.37(3), and 0.81(15), respectively. Note that $\alpha_{Fe} = 0.81(15)$ for FeSe$_{1-x}$ exceeds substantially the universal BCS value $\alpha_{BCS} \equiv 0.5$. In the other studies Shirage et al.\textsuperscript{26,27} have reported a negative $\alpha_{Fe} = -0.18(3)$ and $\alpha_{Fe} = -0.02(4)$ for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ ($T_c \approx 38$ K) and SmFeAsO$_{1-y}$ ($T_c \approx 54$ K), respectively. The negative Fe-IE exponents were also reported recently by Tsuge and coworkers for FeSe$_{0.35}$Te$_{0.65}$ ($T_c \approx 15$ K, $\alpha_{Fe} = -0.54$) and Ca$_{0.4}$Ni$_{0.6}$Fe$_2$As$_2$ ($T_c \approx 34$ K, $\alpha_{Fe} = -0.19$)\textsuperscript{29}. Note that the sín changed isotope effect is unlikely to stem from different pairing mechanisms going to be realized in different Fe-based superconductors. Especially, in the case of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$, when nominally identical samples exhibit once a positive\textsuperscript{25} and next a negative isotope exponent\textsuperscript{26}.

The main purpose of the present study is to show that the very controversial results for Fe-IE on $T_c$ are caused by small structural changes occurring simultane-
ously with the Fe isotope exchange. We demonstrate that the Fe-IE exponent on $T_c$ needs to be decomposed into the one related to the structural changes ($\alpha_{\text{int}}$) and the genuine (intrinsic one, $\alpha_{\text{str}}$) to result in:

$$\alpha_{\text{Fe}} = \alpha_{\text{int}} + \alpha_{\text{str}}.$$

The validity of such decomposition is further confirmed by the fact that $\alpha_{\text{int}}$ coincides with the Fe-IE exponent on the characteristic phonon frequency $\omega_{\text{ph}}$ as is observed in EXAFS and Raman experiments.\textsuperscript{31,32} The value of $\alpha_{\text{int}}$ was found to be the same for representatives of various families of Fe-based superconductors and it stays in the range of $\alpha_{\text{int}} \sim 0.3 - 0.4$ in good agreement with the theory prediction of Bussmann-Holder et al.\textsuperscript{33}

The paper is organized as follows. In Section II we demonstrate the influence of the Fe isotope exchange on the crystal structure. As an example, FeSe\textsubscript{1-x} Fe-based HTS with $T_c \simeq 8$ K is considered. It is shown that the substitution of natural Fe (containing $\approx 92\%$ of $^{56}\text{Fe}$) by its lightest $^{54}\text{Fe}$ isotope leads not only to a shift of $T_c$, but affects also the structural parameters such as the lattice parameters $a$, $b$, and $c$, the lattice volume $V$, the distance between the Se atom and Fe plane, and the Se height $h_{\text{Se}}$. Results presented in this section are adapted from Ref.\textsuperscript{28}. In Section III the currently available Fe isotope effect data on the superconducting transition temperature $T_c$ for various Fe-based HTS were reanalyzed by separating the measured Fe-IE exponent $\alpha_{\text{Fe}}$ into a structural and an intrinsic (unrelated to the structural changes) components. By taking structural corrections into account we infer that the value of the genuine Fe-IE exponent is close to $\alpha_{\text{int}} \sim 0.3 - 0.4$. The results presented in Section III are partially adapted from Ref.\textsuperscript{34}. The conclusions follow in Section IV.

II. Fe ISOTOPE EFFECT ON $T_c$ AND THE CRYSTAL STRUCTURE OF FeSe\textsubscript{1-x}

In this section the $^{56}\text{Fe}/^{54}\text{Fe}$ isotope effects on the superconducting transition temperature and the crystal structure of the iron-chalcogenide superconductor FeSe\textsubscript{1-x} are described.

The preparation procedure for $^{54}\text{Fe}/^{54}\text{Fe}$ isotope submitted FeSe\textsubscript{1-x} powder samples is given in Ref.\textsuperscript{28}. The Fe-IE on the structural properties and the transition temperature $T_c$ were studied in neutron powder diffraction (NPD) and magnetization experiments, respectively.

A. Fe isotope effect on the crystal structure of FeSe\textsubscript{1-x}

The refined structural parameters at $T = 250$ K and 5 K obtained in neutron powder diffraction experiments are summarized in Table I. The results of NPD measurements imply that the substitution of $^{56}\text{Fe}$ by $^{54}\text{Fe}$ 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\textsubscript{4}Se pyramid (see Fig. 1a). As is shown in Fig. 1b, for temperatures below 100 K the Se atom is located closer to the Fe plane in $^{54}\text{FeSe}_{1-x}$ than in $^{56}\text{FeSe}_{1-x}$.

| $T = 250$ K | $T = 5$ K |
|------------------|------------------|
| $^{54}\text{FeSe}_{1-x}$ | $^{56}\text{FeSe}_{1-x}$ |
| $^{54}\text{FeSe}_{1-x}$ | $^{56}\text{FeSe}_{1-x}$ |
| Space group | $P4/nmm$ | $Cmcm$ |
| Se content | 0.975(5) | 0.975(4) | fixed to 0.975 |
| $a$(Å) | 3.77036(3) | 3.76988(5) |
| $b$(Å) | 5.51619(9) | 5.51637(9) |
| $c$(Å) | 156.883(3) | 156.797(3) |
| Volume ($Å^3$) | 155.438(5) | 155.424(5) |
| $z$−Se | 0.2319(2) | 0.2326(0.3) |
| $z$−Se | 0.2321(2) | 0.2322(3) |

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.\textsuperscript{35}, various samples of $^{56}\text{FeSe}_{1-x}$ with $1-x \simeq 0.98$ and $T_c \simeq 8.2$ K indeed exhibit the same lattice parameters within the experimental error.

B. Fe isotope effect on $T_c$ of FeSe\textsubscript{1-x}

The Fe-IE on the transition temperature $T_c$ was studied by means of magnetization experiments. In order to avoid artifacts and systematic errors in the determination of the isotope shift of $T_c$, a statistical study were performed: i.e. the series of $^{54}\text{FeSe}_{1-x}/^{56}\text{FeSe}_{1-x}$ samples synthesized exactly at the same way (the same thermal history, the same amount of Se in the initial composition) were investigated.

The magnetization experiments were conducted for six $^{54}\text{FeSe}_{1-x}$ and seven $^{56}\text{FeSe}_{1-x}$ samples, respectively. Figure 2 shows an example of zero-field cooled (ZFC) magnetization curves for a pair of $^{54}\text{FeSe}_{1-x}/^{56}\text{FeSe}_{1-x}$ samples ($M_{\text{norm}}$ was obtained after subtracting the small paramagnetic offset $M_{\text{mag}}$ measured at $T > T_c$ and further normalization of the obtained curve to the value at $T = 2$ K, see Fig. 1 in Ref.\textsuperscript{35} 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 the inset of Fig. 2. 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
the data presented in Fig. 2 by means of Eq. 1 leads to

as large as $\alpha_{BCS}$ value $\alpha_{BCS}$ $\approx 0.5$ as well as more than twice as large as $\alpha_{Fe}$ $\approx 0.35$ reported for SmFeAsO$_{0.85}$F$_{0.15}$ and Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. We want to emphasize, however, that our structural refined NPD data suggest that part of the large Fe-IE exponent $\alpha_{Fe} = 0.81(15)$ may result from the tiny structural changes occurring due to $^{54}\text{Fe}/^{56}\text{Fe}$ substitution.

C. The structural and the intrinsic contributions to the Fe-IE in FeSe$_{1-x}$

The Fe-IE exponent $\alpha_{Fe} = 0.81(15)$ obtained for FeSe$_{1-x}$ iron-chalcogenide superconductor is larger than the BCS value $\alpha_{BCS} \approx 0.5$ as well as more than twice as large as $\alpha_{Fe}$ $\approx 0.35$ reported for SmFeAsO$_{0.85}$F$_{0.15}$ and Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. We want to emphasize, however, that our structural refined NPD data suggest that part of the large Fe-IE exponent $\alpha_{Fe} = 0.81(15)$ may result from the tiny structural changes occurring due to $^{54}\text{Fe}/^{56}\text{Fe}$ substitution.

An estimate of the structural contribution to the Fe-IE exponent in FeSe$_{1-x}$ can be made based on the observed proportionality between $T_c$ and the crystal lattice constant $a$ for the 11 family FeSe$_{1-y}$Te$_y$. Assuming the relation $T_c$ vs. $a$ holds for FeSe$_{1-x}$ one obtains from the data presented in Ref. 28 for $y \leq 0.5$ the relation $\Delta T_c^a/(\Delta a/a) \approx 6$ K/%. With $(\Delta a + \Delta b)/(a+b) = 0.0195(14)%$ (see Table I and Ref. 28) this results in a structural shift of $T_c$ of $\Delta T_c^\text{str} \approx 0.1$ K. Taking this correction into account yields a rough estimate of the structural and the intrinsic Fe-IE exponent of $\alpha_{Fe}^\text{str} \approx \alpha_{Fe}^\text{int} \approx 0.4$. Note that the value of $\alpha_{Fe}^\text{int}$ $\approx 0.4$ is comparable with $\alpha_{Fe} = 0.35$ reported for SmFeAsO$_{0.85}$F$_{0.15}$ and Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$.

We want to stress, that the "structural" contribution into the Fe-IE exponent in FeSe$_{1-x}$ consists of both: a positive and negative parts. Indeed, in FeSe$_{1-x}$ a decrease of the Se height caused by compression of the FeSe pyramid (see Fig. 1b) b) leads to an increase of $T_c$ by $\Delta T_c^\text{str}/(\Delta h_{Se}/h_{Se}) \approx 3.4$ K/%. In contrast, an increase of the Se(Fe)-Se(Fe) angle in the FeSe$_{1-y}$Te$_y$ family (angle $\beta$ in our notation, see Fig. 1a) results for $y \leq 0.5$ in a decrease of $T_c$ by $\Delta T_c^\beta/(\Delta \beta/\beta) \approx 2.9$ K/%. Based on the structural data presented in Fig. 1 and Table I one obtains $\Delta h_{Se}/h_{Se} = 0.22(8)%$ and $\Delta \beta/\beta = -0.13(4)$%, leading to $\Delta T_c^\text{str} = 0.7(3)$ K and $\Delta T_c^\beta = -0.4(2)$ K (in this estimate the values of $h_{Se}$ were averaged over the temperature regions denoted as solid lines in Fig. 1b). Bearing in mind that all Fe-based HTS are similarly sensitive to structural changes as FeSe$_{1-x}$ (see, e.g., Refs. 30-33) we conclude that
depending on the particular structural changes caused by the Fe isotope substitution, the shift of the transition temperature $T_c$ could be either positive, negative or may stay at zero. Which particular case is going to be realized would require precise studies of the structural properties for each individual isotope experiment.

III. GENUINE (INTRINSIC) AND STRUCTURAL ISOTOPE EFFECTS IN Fe-BASED HTS

The observation of tiny but not negligible isotope effect on the crystal structure observed in FeSe$_{1-x}$ Fe-based HTS reported in the previous section requires to separate the Fe-IE exponent on $T_c$ into the genuine (intrinsic) and the structural components (see Eq. 2). In fact, the superconductivity in all Fe-based HTS is intimately related to small structural changes as reported in various works. As an example the strong nonlinear dependence of the superconducting transition temperature on the anion atom height ($h_{An}$, An=As, P, or Se) with a sharp maximum of $T_c$ at $h_{An} \approx 1.38$ Å, was reported by Mizuguchi et al.\textsuperscript{[28]} (see Fig. 4).

![Figure 3: Dependence of the superconducting transition temperature $T_c$ on the height of the anion atom ($h_{An}$, An=As, Se, P) for various families of Fe-based HTS, after Mizuguchi et al.\textsuperscript{[28]} The closed symbols represent the samples which are relevant for the present study. The lines are guided for the eye. The red (blue) area represents part of $T_c$ vs. $h_{An}$ diagram where $T_c$ increases (decreases) with increasing $h_{An}$.](image)

A. Summary of Fe-IE measurements on the transition temperature $T_c$

The results of Fe-IE measurements of $T_c$ for various Fe-based HTS’s obtained up to date are summarized in Table I and Fig. 4a. In order to account for the structural changes caused by the Fe isotope exchange we have also included in Table I the $c$-axis lattice constants as they measured for the pairs of Fe isotope substituted samples. The choice of the $c$-axis lattice constant as the relevant quantity in deriving the structural isotope effect might appear to be rather arbitrary since $T_c$ is influenced by all structural details, namely tetrahedral angle, $a$-axis lattice constant, internal bond lengths, etc. However, the $c$-axis lattice constant provides a very sensitive probe since its compression(expansion) is directly accompanied by the corresponding variation of the distance from the Fe-planes to the above(below) lying anions which, in turn, is a well characterized property for many Fe-based compounds.\textsuperscript{[28]} A survey of the literature shows that the proportionality between the anion atom height and the $c$-axis lattice constant indeed holds for various families of Fe-based HTS considered in the present study.\textsuperscript{[29,41,42]}

From Table I it follows that in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ and SmFeAsO$_{0.85}$F$_{0.15}$ studied in Ref. 23\textsuperscript{[29]} the $c$-axis constants are the same within the experimental error for both isotopically substituted sets of the samples. In FeSe$_{1-x}$\textsuperscript{[28]} the $c$-axis constant is larger, while in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$\textsuperscript{[26]} it is smaller for the sample with the heavier Fe isotope. In SmFeAsO$_{1-y}$, studied by Shirage et al.\textsuperscript{[27]} both $c$-axis lattice constants seem to coincide within the experimental resolution. However, since the difference between them is 1.5 times larger than one standard deviation, it is conceivable to attribute an increase in the $c$-axis lattice constant in SmFeAsO$_{1-y}$ with the heavier Fe isotope. It should also be noted here that the accuracy in lattice constants determination for Ca$_{0.4}$Na$_{0.6}$Fe$_2$As$_2$ from Ref. 30 is from one to two orders of magnitude worse than it is reported for other isotope substituted samples, and no structural data were reported for FeSe$_{0.35}$Te$_{0.65}$ in Ref. 24\textsuperscript{[29]}

The use of the empirical $T_c$ vs. $h_{An}$ relation from Ref. 38\textsuperscript{[38]} combined with the intrinsic relation of the proportionality between the $c$-axis constant and the anion atom height ($\Delta c \propto h_{An}$, see Refs. 37\textsuperscript{[37]},41\textsuperscript{[41]},42\textsuperscript{[42]} enables us to determine the sign of the structurally related shift of $T_c$ induced by isotopic exchange. By following Mizuguchi et al.\textsuperscript{[28]} (see also Fig. 4) the sign of $(\Delta T_c/T_c)/(\Delta h_{An}/h_{An})$ is positive for SmFeAsO(F) as well as for various Fe-based HTS belonging to FeFeAsO(F) family (Re=Nd, Ce, La) and negative for (BaK)Fe$_2$As$_2$, (CaNa)Fe$_2$As$_2$, FeSe, and FeSe$_{1-x}$. Consequently the change of the $c$-axis constant caused by Fe isotope substitution as presented in Table I results in an additional structurally related shift of $T_c$, being positive for FeSe$_{1-x}$\textsuperscript{[28]} negative for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ and SmFeAsO$_{0.85}$F$_{0.15}$\textsuperscript{[28]} and close to 0 for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ and SmFeAsO$_{0.85}$F$_{0.15}$\textsuperscript{[28]} Note that for the lack of pure(absent) structural data, such estimate is not possible to be made for Ca$_{0.4}$Na$_{0.6}$Fe$_2$As$_2$ and FeSe$_{0.35}$Te$_{0.65}$ from Ref. 20\textsuperscript{[20]}

We want to emphasize that the above mentioned discussion allows only to determine the sign of the structurally related isotope effect but not its absolute value. The reasons are the following. (i) The relative change of the $c$-axis constant is proportional, but not identical to the one of $h_{An}$. As an example, $^{56}$Fe to $^{54}$Fe isotope substitution in FeSe$_{1-x}$ leads to an increase of the $c$-axis...
constant by approximately 0.02%, while the change of the Se height amounts to ten times higher value $\sim 0.22\%$ (see Table I, Fig. 1b, and Ref. [28]). (ii) The height of the anion atom is clearly not the only parameter which is crucial for $T_c$ of Fe-based HTS as already mentioned above.

The analysis of the structural data together with the dependence of $T_c$ on the $a$-axis lattice constant in FeSe$_{1-x}$ as presented in Section III was allowing to extract the “structural” Fe isotope effect exponent $\alpha_{Fe}^{str} \approx 0.4$ for $^{56}$Fe to $^{54}$Fe substituted FeSe$_{1-x}$ samples. The absence of precise structural data for the samples studied in Refs. [23,27,29,30] complicates their analysis. However, a zero, within the experimental accuracy, Fe isotope shift of the $c$-axis lattice constant for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ as reported by Liu et al. in Ref. [25] is a clear indication that no structural effect is present for this particular set of the samples. Consequently, the negative isotope effect exponent $\alpha_{Fe} \approx -0.18$ obtained for nominally identically Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ by Shirage et al. stems from summing both effects, i.e., $-0.18(\alpha_{Fe}) = 0.55(\alpha_{Fe}^{int}) - 0.52(\alpha_{Fe}^{str})$, see Eq. (2). The similar analysis by comparing SmFeAsO(F) Fe-IE exponents from Refs. [23] and [27] results in $\alpha_{Fe}^{str} \approx -0.35$ for SmFeAsO$_{1-y}$ from Ref. [27]. It is worth to notice, however, that the SmFeAsO(F) samples studied in Refs. [23] and [27] have different doping levels (different $T_c$’s, see Table II and Fig. 4(a)).

B. The genuine Fe-IE exponent via phonon frequency measurements

The BCS expression for the superconducting transition temperature $T_c$ relates it to the characteristic phonon frequency $\omega_{ph}$ and the coupling constant $\lambda$ via:

$$T_c \propto \omega_{ph} \exp(-1/\lambda).$$

(3)

The consequences of this equation are two fold. First of all, since the coupling constant $\lambda$ is independent of the ion mass $M$ (see e.g. Ref. [14]) and the characteristic phonon frequency $\omega_{ph}$ is proportional to $1/\sqrt{M}$, as a function of any harmonic oscillator, $\alpha_{BCS}$ becomes equal exactly to 0.5. Note that the Coulomb repulsion and the anharmonicity of phonons, which are not considered in Eq. (3) would lead to smaller $\alpha$ values. Second, due to direct proportionality between $T_c$ and $\omega_{ph}$ the isotope exponents on both these quantities are equal to the each other:

$$\alpha = -\frac{\Delta T_c/T_c}{\Delta M/M} \equiv -\frac{\Delta \omega_{ph}/\omega_{ph}}{\Delta M/M}. \quad (4)$$

Currently we are aware of two experimental works where the Fe-IE on $\omega_{ph}$ was studied by means of EXAFS and Raman techniques on (BaK)Fe$_2$As$_2$, SmFeAsO$_{0.65}$, and SmFeAs$_{0.77}$H$_{0.12}$ Fe-based HTS. The corresponding $\alpha_{Fe}^{ph}$’s are shown in Fig. 1b together with presently obtained $\alpha_{Fe}^{int}$’s (see Section IIIA and Table II). Remarkably enough both sets of Fe-IE exponents stay quite close to the each other with $\alpha_{Fe}^{int} \approx \alpha_{Fe}^{ph} \approx 0.35 \pm 0.07$.

C. Isotope effect within the multiple gap scenario of Fe-based HTS

Bussmann-Holder et al. investigated a multiple gap scenario of superconductivity in Fe-based HTS with the aim to search for possible sources of the isotope effect on $T_c$. Typical phonon-mediated scenarios were contrasted to polaronic effects and found to have very different impacts on the isotope effect. While phonon-mediated superconductivity slightly suppresses the isotope effect as compared to the BCS value $\alpha_{BCS} \equiv 0.5$, polaronic effects can largely enhance it. The scenario of electron-phonon mediated superconductivity within the dominant gap channel predicts a $T_c$ independent isotope effect with the $\alpha$ value being slightly smaller than 0.5. This agrees rather well with that observed for FeSe$_{1-x}$ (BaK)Fe$_2$As$_2$, SmFeAsO$_{0.65}$, and SmFeAs$_{0.77}$H$_{0.12}$ Indeed, for
FIG. 4: (a) Fe isotope effect exponent $\alpha_{Fe}$ as a function of the superconducting transition temperature $T_c$ for the samples considered in the present study: Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ and SmFeAsO$_{0.85}$F$_{0.15}$ Ref. 22, Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ Ref. 20, SmFeAsO$_{1-x}$Ref. 27, FeSe$_{1-x}$, Ref. 25, FeSe$_{0.35}$Te$_{0.65}$ Ref. 25, and Ca$_4$Na$_{8}$Fe$_2$As$_2$ Ref. 21. $\alpha_{BCS} \equiv 0.5$ denotes the BCS value for electron-phonon mediated superconductivity. (b) The “intrinsic” $\alpha_{int}^{Fe}$ (red circles) and the phonon $\alpha_{ph}^{Fe}$ (blue circles) Fe isotope effect exponents as obtained in the present study and the EXAFS and Raman experiments. The grey area denotes the region of 0.3 $\leq \alpha \leq$ 0.4. See text for details.

these particular samples, which are belong to 3 different families of Fe-based HTS and have $T_c$’s ranging from 8 to 54 K, the “intrinsic” Fe isotope exponent is almost constant with $\alpha_{int}^{Fe} \sim 0.3 - 0.4$, see Table III and Fig. IIIb.

IV. CONCLUSIONS

The purpose of the present study was two-fold. First, by presenting results obtained on FeSe$_{1-x}$ iron-chalcogenide superconductor it was demonstrated that the tiny changes of the structural parameters caused by Fe isotope substitution are clearly contributing to the resulting Fe-IE exponent on the transition temperature $T_c$. Depending on the particular changes caused by the Fe isotope substitution, the ”structurally” related shift of the transition temperature $T_c$ could be either positive, negative or stays at zero. Such effects may help to clarify or even be the origin of the previously reported controversial results$^{25,30}$.

Second, the currently available Fe isotope effect data on the superconducting transition temperature $T_c$ for various Fe-based HTS were analyzed by separating the measured Fe-IE exponent $\alpha_{Fe}$ into a structural ($\alpha_{Fe}^{str}$) and an intrinsic (unrelated to the structural changes, $\alpha_{Fe}^{int}$) components. The validity of decomposition the Fe-IE exponent $\alpha_{Fe}$, was further confirmed by the fact that $\alpha_{Fe}^{int}$ almost coincides with the Fe-IE exponent on the characteristic phonon frequencies as observed in recent EXAFS and Raman experiments$^{31,32}$. We infer that the value of the genuine Fe-IE exponent is close to $\alpha_{Fe}^{int} \sim 0.3 - 0.4$ for compounds having $T_c$ ranging from 8 to 54 K and belonging to at least three different families of Fe-based HTS.

V. ACKNOWLEDGMENTS

The author acknowledges the broad and successful collaboration with people without whom this work could not be performed: Markus Bendele, Hugo Keller, Annette Bussmann-Holder, Kazimierz Conder, Ekaterina Pomjakushina, and Volodya Pomjakushin. The special thank goes to Karl Alex Müller and Hugo Keller who were initiated my interest to the isotope effect studies.

* Corresponding author: rustem.khasanov@psi.ch

1 E. Maxwell, Phys. Rev. 78, 477 (1950).
2 C.A. Reynolds, B. Serin, W.H. Wright, and L.B. Nesbitt, Phys. Rev. 78, 487 (1950).
3 C.P. Poole, Handbook of Superconductivity, Academic press, 24-28 Oval Road, London, (2000).
4 W. Buckel and B. Strizker, Phys. Letters 43A, 403 (1973).
5 J.E. Schirber and C.J.M. Northrup, Jr., Phys. Rev. B 10, 3818 (1974).
6 M. Yuossoff, B.K. Rao, and P. Jena, Sol. State. Commun. 94, 549 (1995).
7 J.A. Schlueter, A.M. Kini, B.H. Ward, U. Geiser, H.H. Wang, J. Mohtasham, R.W. Winter and G.L. Gard, Physica C 351, 261 (2001).
8 M.H. Whangbo, J.M. Willimas, A.J. Schultz, T.J. Emge, and M.A. Beno, J. Am. Chem.Soc., 109, 90 (1997).
9 A. Stucky, G. Scheerer, Z. Ren, D. Jaccard, J.-M. Prounirol, C. Barreteau, E. Giannini, D. van der Marel, arXiv:1610.10045.
10 B. Batlogg, G. Kourouklis, W. Weber, R.J. Cava, A. Jayaraman, A.E. White, K.T. Short, L.W. Rupp, and E.A. Rietman, Phys. Rev. Lett. 59, 912 (1987).
11 J.P. Franck, J. Jung, M.A-K. Mohamed, S. Gygax, and G.I. Sproule, Phys. Rev. B 44, 5318 (1991).
12 J.P. Franck, in Physical Properties of High Temperature Superconductors IV, edited by D. M. Ginsberg (World Sci-
J.L. Tallon, R.S. Islam, J. Storey, G.V.M. Williams, and R.H. Liu, T. Wu, G. Wu, H. Chen, X.F. Wang, Y.L. Xie, R. Khasanov, A. Shengelaya, K. Conder, E. Morenzoni, I.M. Savić, and H. Keller, J. Phys.: Condens. Matter 13, R569 (2001).

R. Khasanov, A. Shengelaya, K. Conder, E. Morenzoni, I.M. Savić, and H. Keller, J. Phys.: Condens. Matter 15, L17 (2003).

R. Khasanov, A. Shengelaya, E. Morenzoni, M. Angst, K. Conder, I. M. Savić, D. Lampakis, E. Liarokapis, A. Tatsi, and H. Keller, Phys. Rev. B 68, 220506(R) (2003).

R. Khasanov, A. Shengelaya, E. Morenzoni, K. Conder, I.M. Savić, and H. Keller, J. Phys.: Condens. Matter 16, S4439 (2004).

R. Khasanov, D. G. Eschenko, H. Luetkens, E. Morenzoni, T. Prokscha, A. Suter, N. Garifianov, M. Malí, J. Roos, K. Conder, and H. Keller, Phys. Rev. Lett. 92, 057602 (2004).

R. Khasanov, A. Shengelaya, K. Conder, E. Morenzoni, I. M. Savić, J. Karpinski, and H. Keller, Phys. Rev. B 74, 064504 (2006).

R. Khasanov, A. Shengelaya, D. Di Castro, D.G. Eschenko, I.M. Savić, K. Conder, E. Pomjakushina, J. Karpinski, S. Kazakov, and H. Keller, Phys. Rev. B 75, 060505(R) (2007).

R. Khasanov, S. Strässle, K. Conder, E. Pomjakushina, A. Bussmann-Holder, and H. Keller, Phys. Rev. B 77, 104530 (2008).

J.L. Tallon, R.S. Islam, J. Storey, G.V.M. Williams, and J.R. Cooper, Phys. Rev. Lett. 94, 237002 (2005).

X.-J. Chen, B. Liang, C. Ulrich, C.-T. Lin, V.V. Struzhkin, Z. Wu, R.J. Hemley, H.-k. Mao, and H.-Q. Lin, Phys. Rev. B 76, 140502 (2007).

R. Khasanov, A. Shengelaya, D. Di Castro, E. Morenzoni, A. Maisuradze, I.M. Savić, K. Conder, E. Pomjakushina, A. Bussmann-Holder, and H. Keller, Phys. Rev. Lett. 101, 077001 (2008).

R.H. Liu, T. Wu, G. Wu, H. Chen, X.F. Wang, Y.L. Xie, J.J. Yin, Y.J. Yan, Q.J. Li, B.C. Shi, W.S. Chu, Z.Y. Wu, and X.H. Chen, Nature 459, 64 (2009).

P.M. Shirage, K. Kihou, K. Miyazawa, C.-H. Lee, H. Kito, H. Eisaki, T. Yanagisawa, Y. Tanaka, and A. Iyo, Phys. Rev. Lett. 103, 257003 (2009).

P.M. Shirage, K. Miyazawa, K. Kihou, H. Kito, Y. Yoshida, Y. Tanaka, H. Eisaki, and A. Iyo, Phys. Rev. Lett. 105, 037004 (2010).

R. Khasanov, M. Bendele, K. Conder, H. Keller, E. Pomjakushina, and V. Pomjakushin, New J. Phys. 12, 073024 (2010).

Y. Tsuge, A. Iyo, Y. Tanaka, H. Eisaki, and T. Nishio, Physics Procedia 36, 731 (2012).

Y. Tsuge, T. Nishio, A. Iyo, Y. Tanaka, and H. Eisaki, Journal of Physics: Conference Series, 507, 012037 (2014).

W. Chu, J. Cheng, S. Chu, T. Hu, A. Marcelli, X. Chen, and Z. Wu, Scientific Reports 3, 1750 (2013).

B. Singh, P.M. Shirage, A. Iyo, and P. Kumar, AIP Advances 6, 105310 (2016).

A. Bussmann-Holder, A. Simon, H. Keller, and A.R. Bishop, J. Supercond. Nov. Magn. 24, 1099 (2011).

R. Khasanov, M. Bendele, A. Bussmann-Holder, H. Keller, Phys. Rev. B 82, 212505 (2010).

E. Pomjakushina, K. Conder, V. Pomjakushin, M. Bendele, and R. Khasanov, Phys. Rev. B 80, 024517 (2009).

K. Horigane, H. Hiraka, and K. Ohoyama, J. Phys. Soc. Jpn. 78, 074718 (2009).

Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi and Y. Takano, J. Phys. Soc. Jpn. 78, 074712 (2009).

Y. Mizuguchi, Y. Haras, K. Deguchi, S. Tsuda, T. Yamaguchi, K. Takeda, H. Kotegawa, H. Tou, and Y. Takano, Supercond. Sci. Technol. 23, 054103 (2010).

S. Margadonna, Y. Takabayashi, M.T. McDonald, M. Brunelli, G. Wu, R.H. Liu, X.H. Chen, and K. Prasides, Phys. Rev. B 79, 014503 (2009).

J. Zhao, Q. Huang, C. de la Cruz, S. Li, J.W. Lynn, Y. Chen, M.A. Green, G.F. Chen, G. Li, Z. Li, J.L. Luo, N.L. Wang, and P. Dai, Nature Materials 7, 953 (2008).

M. Rotter, M. Pangerl, M. Tegel, and D. Johrendt, Angew. Chem. Int. Ed. 47, 7949 (2008).

T.M. McQueen, Q. Huang, V. Ksenofontov, C. Felser, Q. Xu, H.W. Zandbergen, Y.S. Hor, J. Allred, A.J. Williams, D. Qu, J. Checkelsky, N.P. Ong, and R.J. Cava, Phys. Rev. B 79, 014522 (2009).

M. Tinkham, Introduction to Superconductivity, Krieger Publishing company, Malabar, Florida, 1975.

A.S. Alexandrov, Theory of Superconductivity: From Weak to Strong Coupling, Institute of Physics Publishing, Bristol, 2003.