Inverse Iron Isotope Effect on the Transition Temperature of the (Ba, K)Fe_2As_2 Superconductor

Parasharam M. Shirage,[1,*] Kunihiro Kihou,[1] Kiichi Miyazawa,[1,2] Chul-Ho Lee,[1,3] Hijiri Kito,[1,3] Hiroshi Eisaki,[1,3]
Takashi Yanagisawa,[1] Yasumoto Tanaka,[1] and Akira Iyo[1,2,3,†]
[1]National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan
[2]Department of Applied Electronics, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-3510, Japan
[3]JST, Transformative Research Project on Iron Pnictides (TRIP), 5, Sanbancho, Chiyoda, Tokyo 102-0075, Japan

(Received 20 March 2009; published 17 December 2009)

We report that the (Ba, K)Fe_2As_2 superconductor (transition temperature, $T_c \sim 38$ K) has an inverse iron isotope coefficient $\alpha_{\mathrm{Fe}} = -0.18(3)$ (where $T_c \sim M^{-\alpha_{\mathrm{Fe}}}$ and M is the iron isotope mass); i.e., the sample containing the large iron isotope mass depicts a higher T_c. Systematic inverse shifts in T_c were clearly observed between the samples using three types of Fe isotopes (^{54}Fe, natural Fe, and ^{57}Fe). This indicates the first evidence of the inverse isotope effect in high-T_c superconductors. This anomalous mass dependence on T_c implies an exotic coupling mechanism in Fe-based superconductors.

DOI: 10.1103/PhysRevLett.103.257003 PACS numbers: 74.62.Bf, 74.25.Kc, 74.70.Dd

The discovery of superconductivity with a T_c of 26 K in the Fe-based oxypnictide $LaFeAsO_{1-x}F_x$ has provided a new paradigm for exploring new high-T_c superconductors [1,2]. Although several recent studies suggest that superconductivity in the iron-based system is unconventional and that the suggested pairing mechanism is not due to the phonon [3–5], the mechanism of superconductivity is currently in dispute. In conventional superconductors, the strong effect of a changing ion mass M on T_c implies that lattice vibrations (phonons) play an important role in the microscopic mechanism of superconductivity [6,7]. The isotope exponent α is defined by $T_c \sim M^{-\alpha}$, where M is the isotopic mass. In the classical form of BCS theory [8], α is equal to 0.5. For simple low-T_c metals like Hg, Pb, Sn, and Zn, the isotope coefficient is found experimentally to be close to 0.5. (Ba, K)BiO_3 ($T_c \sim 30$ K), MgB_2 ($T_c \sim 40$ K), and CaC_6 ($T_c \sim 11$ K) show large isotope effect coefficients $\alpha_O \approx 0.4$, $\alpha_B \approx 0.3$, and $\alpha_{Ca} \approx 0.5$, respectively [9–12]. Thus the observation of isotope effect on T_c is crucial in suggesting phonon-mediated paring mechanism in superconductors.

Here we report on the iron isotope effect on T_c for the (Ba, K)Fe_2As_2 superconductor ($T_c \approx 38$ K) [13]. Apparent inverse isotope effect has been observed between the samples containing two different iron isotopes. Possible explanation of the inverse isotope effect is also discussed.

We used three sorts of Fe: ^{57}Fe enriched powder (ISOFLEX USA, purity 99.99%), ^{54}Fe enriched powder (ISOFLEX USA, purity 99.99%), and natural Fe powder (^{n}Fe) (Showa Chemical Industry, purity 99.9%). The isotopic mass of the ^{57}Fe, ^{n}Fe, and ^{54}Fe powders are 57.00, 55.85, and 54.01, respectively.

Polycrystalline samples of (Ba, K)Fe_2As_2 were prepared by a high-pressure synthesis method [14]. The sample synthesized from a stoichiometric starting composition of $(Ba_{1-x}K_x)Fe_2As_2$ includes a FeAs impurity phase probably because K and Ba exclude from the samples during heat treatment. This difficulty was overcome by using the 50% excess of Ba and K for the starting composition, i.e., $(Ba_{0.5}K_{0.5})_{1.5}Fe_2As_2$. Precursors of BaAs, KAs, and As powder were mixed homogeneously and divided into two equal weights and then mixed with the two different iron isotopes in order to rule out K concentration difference between the two samples which can be a factor to change T_c. The materials were ground by an agate mortar in a glove box. The mixed powders were pressed into pellets. Two pellets were put into a boron nitride (BN) crucible as shown in the inset of Fig. 1to rule out the difference in synthesis temperature and pressure, which can also affect in a variation in the T_c between the samples. The samples were simultaneously heated at about 900 °C under a pressure of about 1 GPa for 1 h. Three combinations of isotopic Fe, ^{n}Fe and ^{57}Fe, ^{57}Fe and ^{54}Fe, and ^{54}Fe and ^{n}Fe, were tested for sample preparation to ensure systematic behavior of T_c. We obtained seven sets of samples ($S1$–$S7$) synthesized in the same conditions except for the iron isotope mass.

Powder x-ray diffraction (XRD) patterns of the samples were measured by using CuK_a radiation. The dc magnetic susceptibility was measured by using a SQUID magnetometer (Quantum Design Magnetic Property Measurement System) under a magnetic field of 5 Oe. The resistivity of the two isotope containing samples was measured simultaneously by a four-probe method (Quantum Design Physical Property Measurement System).

All of the samples are an almost single phase, and difference in lattice parameters between the two samples synthesized simultaneously was small (negligible). The XRD patterns of the sample set $S2$ synthesized using ^{54}Fe and ^{57}Fe isotopic powders, $S2(^{54}Fe)$ and $S2(^{57}Fe)$, are represented in Fig. 1 as a typical example. The lattice parameters of the samples $S2(^{57}Fe)$ and $S2(^{54}Fe)$ are $a = 3.914(1)$ Å, $c = 13.310(1)$ Å and $a = 3.914(1)$ Å, $c = 13.313(1)$ Å, respectively. Judging from the c-axis parameters, actual K concentration x of the samples in

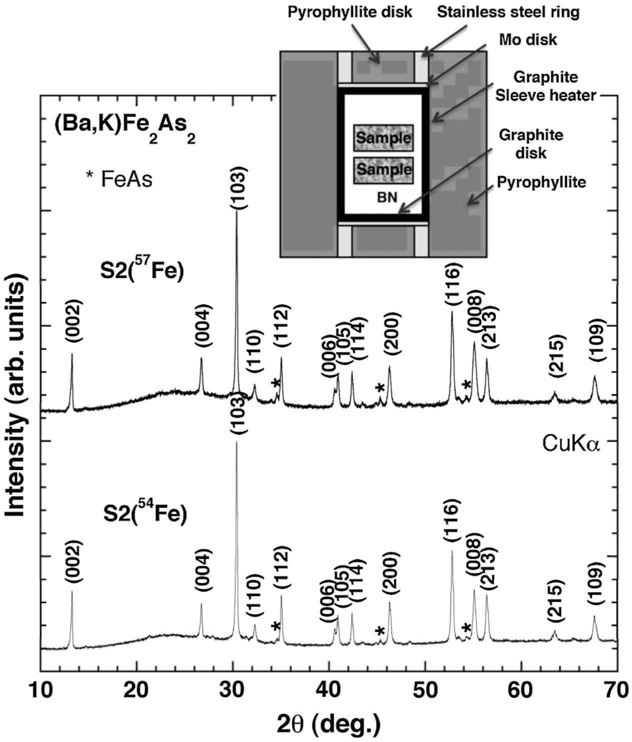

FIG. 1. X-ray diffraction patterns of the samples $S2(^{57}\mathrm{Fe})$ and $S2(^{54}\mathrm{Fe})$ synthesized simultaneously in a BN crucible by high-pressure synthesis technique. The inset shows the sample cell assembly for the high-pressure synthesis method.

$(\mathrm{Ba}_{1-x}\mathrm{K}_x)\mathrm{Fe}_2\mathrm{As}_2$ is about 0.4 [15], where T_c is almost constant against x, which is suitable for verification of the isotope effect. We also confirmed the homogeneity of the samples by using a scanning electron microscope with energy dispersive x-ray spectroscopy analysis, and we detected the $x = 0.40(2)$ throughout the pellet.

Figures 2(a)–2(c) represent the temperature (T) dependence of normalized zero-field cooled (ZFC) susceptibility (χ) for the three types of Fe-isotopic combinations of the samples. The samples demonstrated the χ at 5 K ranging from -0.0154 to -0.0182 emu/g that corresponds to the superconducting volume fraction of 114%–134% without demagnetizing field correction. A clear isotope shift in T_c can be seen in each combination. Surprisingly, the sample containing the larger iron isotope mass depicting higher T_c, indicates the inverse isotope effect. $T_{c(\chi)}$ is determined from the definition as shown in the inset of Fig. 2. Isotope shifts in $T_{c(\chi)}$ ($\Delta T_{c(\chi)}$) and α_{Fe} of the sample sets $S1$–$S7$ are listed in Table I.

In Fig. 3 the temperature dependent normalized resistivity of the samples $S2(^{57}\mathrm{Fe})$ and $S2(^{54}\mathrm{Fe})$ are shown. It should be noted that the normal state in the normalized resistivity plot almost overlapped each other except in the region of T_c, assuring the same quality of the samples. $T_{c(\rho)}$ is determined by the definition as shown in the inset of Fig. 3. This result also clearly shows that the sample

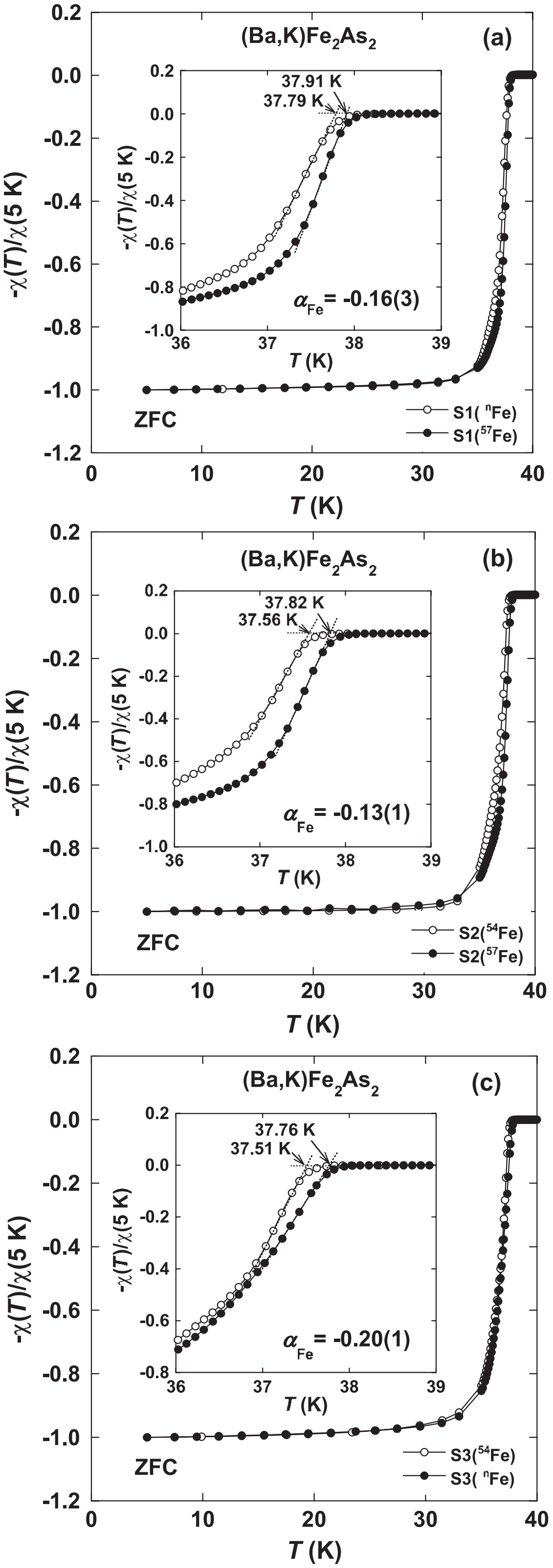

FIG. 2. (a)–(c) Temperature (T) dependence of susceptibility (χ) of the three sample sets using three different combinations of the isotopic Fe: (a) $S1(^{n}\mathrm{Fe})$ and $S1(^{57}\mathrm{Fe})$, (b) $S2(^{57}\mathrm{Fe})$ and $S2(^{54}\mathrm{Fe})$, and (c) $S3(^{54}\mathrm{Fe})$ and $S3(^{n}\mathrm{Fe})$. The χ is normalized at the values of the ZFC curve at 5 K.

TABLE I. Istope shift in $T_{c(\chi)}$ ($\Delta T_{c(\chi)}$) and α_{Fe}. $T_{c(\chi)}$ are determined from the magnetic susceptibility measurements of (Ba, K)Fe_2As_2 samples containing ^{54}Fe, ^{n}Fe, and ^{57}Fe isotopes. The average α_{Fe} is −0.18(3).

	$T_{c(\chi)}$ (K)			$\Delta T_{c(\chi)}$	α_{Fe}
	^{54}Fe	^{n}Fe	^{57}Fe		
*S*1		37.79(1)	37.91(1)	−0.12(2)	−0.16(3)
*S*2	37.56(1)		37.82(2)	−0.26(3)	−0.13(1)
*S*3	37.51(1)	37.76(1)		−0.25(2)	−0.20(1)
*S*4	37.54(1)	37.79(2)		−0.25(2)	−0.20(2)
*S*5	37.32(1)		37.75(1)	−0.43(2)	−0.21(1)
*S*6	37.42(1)		37.77(1)	−0.35(2)	−0.17(1)
*S*7	37.39(1)		37.76(1)	−0.37(2)	−0.18(1)

containing ^{57}Fe has higher T_c than ^{54}Fe. The isotope exponent is estimated to be $\alpha_{\mathrm{Fe}} = -0.22(2)$, which is somewhat larger than that measured by the magnetic susceptibility method, but comparable.

Figure 4 shows the iron isotope mass dependent T_c for the sample sets *S*1–*S*7. The sample containing the larger iron isotope mass invariably showed higher T_c. The results presented here evidently demonstrate that the iron isotope effect coefficient (α_{Fe}) is negative and highly reproducible. The average α_{Fe} of the seven sets of samples is −0.18(3). Our result is contradictory with the earlier report on (Ba, K)Fe_2As_2 ($\alpha_{\mathrm{Fe}} = 0.37$) by Liu *et al.* [16]. They synthesized the samples in a quartz tube from a stoichiometric composition of $(Ba_{0.6}K_{0.4})Fe_2As_2$. The contradiction may result from the difference in K concentration of the samples. In the case of cuprate superconductors, a nearly zero oxygen-isotope effect is observed in the optimally doped state, but an oxygen-isotope effect in the underdoped state is large [17–22]. It will be necessary to measure the α_{Fe} as a function of K concentration.

The inverse isotope effect in (Ba, K)Fe_2As_2 is the first case in high-T_c superconductors [23] and strongly suggests that the superconducting mechanism of the iron-based system is not explained by conventional BCS theory mediated by phonons. On the other hand, it indicates that phonons play some particular role in this superconductivity. The inverse isotope effect can be explained by assuming a competition between the conventional phonon-mediated superconductivity and the unconventional one [possibly mediated by antiferromagnetic (AF) fluctuation] [24,25]. When BCS pair hopping between electron Fermi-surface (FS) and hole FS by AF fluctuation dominates the superconductivity, it reverses the sign of the order parameter between two FS's (it is sometimes designated as the s_{+-} wave). However, there is also a BCS pair hopping between the two FS's by phonons, which does not reverse the sign (s_{++} wave). When the s_{+-} wave is realized, T_c is suppressed with increasing of contribution of phonon, i.e., increasing phonon frequency. It leads to an inverse isotope effect.

This tendency can be reproduced by the weak coupling BCS theory when there are several bosons mediating BCS pairs [26]. We take into account two kinds of pair hopping processes mediated by AF fluctuation and phonon (neglecting contribution from the intra-FS pair hopping). For simplicity, we provide two symmetrical FS's. The T_c can be expressed as follows:

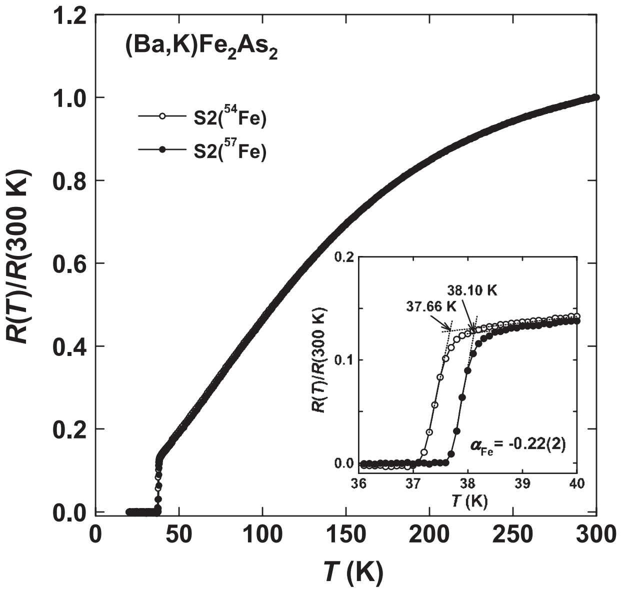

FIG. 3. Temperature (T) dependence of resistivity (ρ) of the sample *S*2(^{57}Fe) and *S*2(^{54}Fe). The Fe isotope exponent is estimated to be $\alpha_{\mathrm{Fe}} = -0.22(2)$.

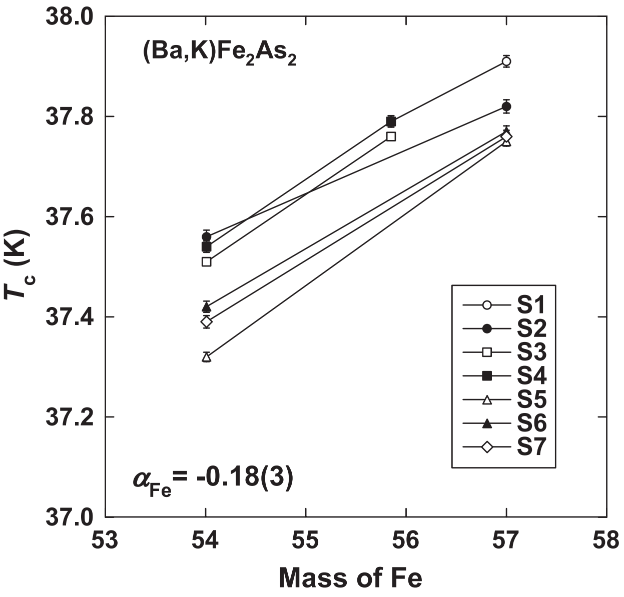

FIG. 4. The iron isotope mass dependence of $T_{c(\chi)}$ for the seven sets of the samples *S*1–*S*7. Fe isotope exponent α_{Fe} is −0.18(3).

$$k_B T_c = 1.13\hbar\omega_{\text{phonon}}\exp\left(-\frac{1}{-\lambda_{\text{ph}} - \frac{1}{\ln(\frac{\omega_{\text{AF}}}{\omega_{\text{phonon}}}) - \frac{1}{\lambda_{\text{AF}}}}}\right).$$

λ_{AF}, ω_{AF}, λ_{ph}, and ω_{phonon} are the dimensionless coupling constants and the cutoff frequencies of the AF fluctuation and phonon, respectively. We provide $\omega_{\text{AF}} > \omega_{\text{phonon}}$, but it is not crucial for the explanation of the inverse isotope effect. Four values are taken as positive values, and the sign of the pair interaction directly reflects the sign in the formula. This formula can be reduced in the case of $\lambda_{\text{AF}} \gg \lambda_{\text{ph}}$ as follows:

$$k_B T_c \approx 1.13\hbar\omega_{\text{AF}}\exp\left(-\frac{1}{\lambda_{\text{AF}}} - \lambda_{\text{ph}}\left\{\ln\left(\frac{\omega_{\text{AF}}}{\omega_{\text{phonon}}}\right) - \frac{1}{\lambda_{\text{AF}}}\right\}^2\right).$$

When the cutoff frequency of the AF fluctuation and phonon is comparable, the inverse isotope effect emerges. It is the consequence of a competition between the AF fluctuation and phonon for the interband BCS pair hopping process.

$\lambda_{\text{ph}}/\lambda^*_{\text{AF}} = 0.14$ reproduces the inverse isotope shift of $\alpha_{\text{Fe}} = -0.18$, where $\lambda^*_{\text{AF}} = \frac{\lambda_{\text{AF}}}{1-\lambda_{\text{AF}}\ln(\omega_{\text{AF}}/\omega_{\text{phonon}})}$.

Providing $\omega_{\text{phonon}} = 350$ K, we deduce $\lambda_{\text{ph}} = 0.07$, $\lambda^*_{\text{AF}} = 0.50$ gives $T_c = 38$ K as reasonable values. (We note that the intraband pair hopping mediated by the phonon cooperates with both interband processes. The details on the theoretical analysis of inverse isotope effect can be found in the report of Yanagisawa *et al.* [27].)

In conclusion, a significant inverse iron isotope effect [$\alpha_{\text{Fe}} = -0.18(3)$] was observed in the (Ba, K)Fe_2As_2 superconductor. Results obtained here suspect that the phonon plays some particular role and implies the exotic coupling mechanism in this superconductivity. Explaining this anomaly will be a key in understanding the mechanism of the Fe-based superconductors and may lead to pioneering the basics in the field of high-T_c superconductivity.

This work was supported by a Grant-in-Aid for Specially Promoted Research (No. 20001004) from The Ministry of Education, Culture, Sports, Science and Technology (MEXT) and JST, Transformative Research Project on Iron Pnictides (TRIP).

---

*paras-shirage@aist.go.jp
†iyo-akira@aist.go.jp

[1] Y. Kamihara *et al.*, J. Am. Chem. Soc. **128**, 10 012 (2006); Y. Kamihara *et al.*, J. Am. Chem. Soc. **130**, 3296 (2008).
[2] G. F. Chen *et al.*, Phys. Rev. Lett. **100**, 247002 (2008); X. H. Chen *et al.*, Nature (London) **453**, 761 (2008).
[3] L. Boeri, O. V. Dolgov, and A. A. Golubov, Phys. Rev. Lett. **101**, 026403 (2008).
[4] A. D. Christianson *et al.*, Nature (London) **456**, 930 (2008).
[5] Y. Nakai *et al.*, J. Phys. Soc. Jpn. **77**, 073701 (2008).
[6] J. P. Franck, in *Physical Properties of High Temperature Superconductors IV*, edited by D. M. Ginsberg (World Scientific, Singapore, 1994), p. 189.
[7] R. Kishore, in *Studies of High Temperature Superconductors*, edited by A. Narlikar (Nova Science Publishers, Commack, NY, 1999), Vol. 29, p. 23.
[8] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[9] D. G. Hinks *et al.*, Nature (London) **335**, 419 (1988).
[10] S. L. Bud'ko *et al.*, Phys. Rev. Lett. **86**, 1877 (2001).
[11] D. G. Hinks, H. Claus, and J. D. Jorgensen, Nature (London) **411**, 457 (2001).
[12] D. G. Hinks *et al.*, Phys. Rev. B **75**, 014509 (2007).
[13] M. Rotter *et al.*, Phys. Rev. B **78**, 020503(R) (2008).
[14] P. M. Shirage *et al.*, Phys. Rev. B **78**, 172503 (2008); P. M. Shirage *et al.*, Physica (Amsterdam) **469C**, 355 (2009); P. M. Shirage *et al.*, Appl. Phys. Express **1**, 081702 (2008).
[15] M. Rotter *et al.*, Angew. Chem., Int. Ed. **47**, 7949 (2008).
[16] R. H. Liu *et al.*, Nature (London) **459**, 64 (2009).
[17] B. Batlogg *et al.*, Phys. Rev. Lett. **58**, 2333 (1987).
[18] D. E. Morris *et al.*, Phys. Rev. B **37**, 5936 (1988).
[19] M. K. Crawford *et al.*, Science **250**, 1390 (1990).
[20] D. J. Pringle, G. V. M. Williams, and J. L. Tallon, Phys. Rev. B **62**, 12 527 (2000).
[21] A. Iyo, Y. Tanaka, and H. Ihara, Physica (Amsterdam) **378–381C**, 298 (2002).
[22] R. Khasanov *et al.*, Phys. Rev. Lett. **101**, 077001 (2008).
[23] Inverse isotope effect is also reported for palladium hydride PdH ($T_c \sim 10$ K) for which the replacement of hydrogen by its heavier isotope deuterium has the reverse effect of raising T_c. This material is belonging to low-T_c material. B. Stritzer and W. Buckel, Z. Phys. **257**, 1 (1972).
[24] K. Kuroki, Phys. Rev. Lett. **101**, 087004 (2008).
[25] I. I. Mazin *et al.*, Phys. Rev. Lett. **101**, 057003 (2008).
[26] K. Yamaji, Solid State Commun. **61**, 413 (1987).
[27] T. Yanagisawa *et al.*, J. Phys. Soc. Jpn. **78**, 094718 (2009).