Radiation Enhancement of Superconducting Critical Temperature of Fe-based HTSCs

Kriti R Sahu¹, Ashish K Mishra², D. Sanyal³, Thomas Wolf⁴, A. Banerjee², V. Ganesan² and Udayan De¹,*

¹Department of Physics, Egna S. S. B. College, Egna, Purna Medinipur, West Bengal; India 721429
²UGC-DAE CSR, Indore-452001, Madhya Pradshesh India
³Variable Energy Cyclotron Centre, 1/AF Bidhannagar, Kolkata 700064, India
⁴Karlsruhe Institute of Technology, Karlsruhe D-76021, Germany

ABSTRACT: High Temperature Superconductivity (HTSC) with Superconducting Critical Temperature (Tc) up to 56 K in Fe Pnictides/Chalcogenide compounds baffled the classical idea that magnetic ions like Fe destroy superconductivity. These Fe-superconductors appear to be better than Cu-oxide HTSCs for making superconducting wires, considering the easier fabricability for Fe-HTSCs, for magnet and other applications, making Fe HTSCs an important group of emerging materials. Fusion and accelerator magnets work in intense radiation environment. So, as a first step, radiation damage of Ba(Fe0.943Co0.057)2As2 single crystal HTSC due to 1.5 MeV Ar⁶⁺ irradiation has been investigated. A peak in the imaginary part (χ") of magnetic susceptibilty indicates Tc. The un-irradiated (UR) sample shows Tc = 15.95 K from its χ" peak. Irradiated Tc from χ" and electrical resistivity measurements are in excellent agreement with magnetic χ" result of radiation enhanced Tc of 24.01 K, which is a new observation. Further studies under high magnetic fields will be discussed. Earlier report for Fe-HTSC films on enhancement of Tc from 18.0K to 18.5K due to 1×10¹⁵ p/cm² irradiation of 190keV protons, support present observation. Physics needs to be investigated further.

KEYWORDS: Fe Pnictide superconductor, ion radiation damage, HTSC, upper critical field, Ba(Fe0.943Co0.057)2As2 single crystals

https://doi.org/10.29294/IJASE.6.S2.2020.11-17 © 2020 Mahendrapublications.com, All rights reserved

1. INTRODUCTION
Zero electrical resistivity and, more importantly, exclusion of magnetic flux on cooling a sample below its Superconducting Critical Temperature (Tc) confirm its entry into the superconducting state[1,2]. Superconductivity was discovered in 1911. Its presenting new surprises like Cu-O based High Temperature Superconductors (HTSCs) in recent decades[3]. Latest surprise is superconductivity including high temperature superconductivity (with Tc up to 56 K) in Fe pnictide(Fe) / chalcogenide (Cn) compounds, with Fe-As or Fe-Te/Se layers as the seat of superconductivity[3-5]. Here, magnetic ions like Fe (or often Ni) is a major component. This shatters the textbook idea that magnetic impurities always destroy electron pairing and superconductivity. Search for pairing mechanism in Fe-HTSCs, most unlikely to be BCS, can be somewhat unearthed by radiation damage experiments. Stronger impetus for radiation modification investigations in Fe-HTSCs come from potential fabrication of Fe-HTSC cables and hence superconducting magnets and devices[6,7]. These may be used in radiation environment of accelerators and fusion reactors. So, an estimate of damage by fast neutrons and ions, and hence the working life of the Fe-HTSC magnets or devices must be made. Expulsion of magnetic flux from the inside of asuperconductor leads to a peak at Tc in the imaginary part of magnetic susceptibility (χ") and a step at Tc in the real part of magnetic susceptibilty (χ'). Here, radiation damage by fast heavy ion beam to Ba(Fe1-xCo)xAs2, x = 0 and 0.057, have been investigated by XRD, Magnetic Susceptibility and Electrical Resistivity Measurements.

2. EXPERIMENTAL OUTLINE
2.1 Single Crystal Sample Preparation, XRD Characterization and Ion Irradiation
The single crystals (SXLs) of Ba(Fe1-xCo)xAs2 were grown[5] by self flux method, using a glassy carbon crucible. After heating Ba(Fe,Co)As at 1:5 mixture to 1160°C in the crucible, it was cooled down very slowly at rates (0.22–0.30 °C/h). On completion of the growth the crucible was tilted to decant away the remaining flux. SXLs were collected from the crucible. XRD of UR samples in FIG.1 shows only 00l reflections from the large face of length 17 – 3mm (length), 1 – 2 mm (width) and 0.2 – 1mm (thickness) samples. This proves the single crystal nature of the samples.Moreover, the peaks show gradual decrease of the lattice parameter c due to increasing Co-substitution: c =13.0314 Å for x=0.00, c = 12.999 Å for x=0.057 & 12.988 Å for x=0.102[8]. Here, ~200 micron thick SKLs have been irradiated at IUAC, New Delhi, India, by 1.5 MeV Ar⁶⁺-beam. The

*Corresponding Author: ude2006@gmail.com
Received: 15.10.2019 Accepted: 11.12.2019 Published on: 27.01.2020

Kriti R Sahu et al.,
International Journal of Advanced Science and Engineering www.mahendrapublications.com
crystals have been characterized first in UR (Un-Radiated) and then in AR (After Radiated) condition.

### 2.2 Electrical Resistivity Measurement

Using a standard DC 4-probe technique, electrical resistivity of our un-radiated and radiated SXL samples have been measured from room temperature down to 2K in a liquid helium cryostat under different magnetic fields (0 to 6 Tesla), applied along c axis direction of the samples. For resistivity measurements, rectangular shaped samples have been cut out with a wire-saw. Electrical contacts for conduction along the large face that turned out from XRD to be ab-plane have been made by attaching thin copper wires with silver epoxy.

### 2.3 Magnetic Susceptibility Measurement

A Vibrating Sample Magnetometer from Quantum Design has been used for measurement down to 2 K, of real and imaginary parts of Magnetic Susceptibility.

### 3. RESULTS AND DISCUSSION

FIG. 1(a) depicts full XRD pattern, with all the observed peaks indexed for Ba(Fe\(_{1-x}\)Co\(_x\))\(_2\)As\(_2\), as a function of irradiation dose (zero to 10\(\times\)10\(^{15}\)Ar-ions/cm\(^2\)). Gradual broadening of the peaks on irradiation can be observed, more clearly in FIG. 1(b), an enlarged view for 004 peak only.

![XRD pattern](https://example.com/xrd_pattern.png)

**FIG. 1:** (a) XRD (x-ray diffraction) pattern of plate-like Single Crystal Ba(Fe\(_{1-x}\)Co\(_x\))\(_2\)As\(_2\), x = 0.057 or 5.7% samples showing only 00l reflections – in UR (Un-radiation) & AR (After radiations, by 1.5 MeV Ar-beam) conditions. Sharp peaks in un-irradiated Ba122 samples (called “Ba5.7Co UR”) become progressively broader after irradiation fluences 0.2\(\times\)10\(^{15}\) (sample “2Ba5.7Co AR”), 2.5\(\times\)10\(^{15}\) (sample “5Ba5.7Co AR”) and 10\(\times\)10\(^{15}\) ions/cm\(^2\). (sample “7Ba5.7Co AR”). (b) XRD in 20 range 27° to 28° showing the 004 peak in details.
FIG. 2. Imaginary part of magnetic susceptibility ($\chi''$ in emu unit) (i) for the un-radiated pure BaFe$_2$As$_2$ (called Ba122 UR sample and indicated by hexagonal: half-filled symbol with olive colour) sample; (ii) un-radiated 5.7% Co doped BaFe$_2$As$_2$ sample (called 2Ba5.7Co UR sample shown by wine-coloured solid spheres; and (iii) 5.7% Co doped sample after radiation to 2.5 × 10$^{15}$ Ar-ions cm$^{-2}$ (called “5Ba5.7Co AR” sample indicated by blue-coloured half-filled diamond symbols.

Graphs for 2 to 300 K have been supplemented by enlarged view of the transitions in the inset. Irradiation, increases (FIG. 4, H=0 graphs) $T_c$ from ~15.6 K to 23.8 K i.e. by 8.2 K in excellent agreement with the magnetic result. We find that the step in $\chi'$ data show same $T_c$ as $\chi''$ peak (unpublished).

X-ray peaks in the un-radiated samples are sharper. They broaden progressively on irradiation to fluences 0.2×$10^{15}$, 2.5×$10^{15}$ and 10×$10^{15}$ Ar-ions/cm$^2$, indicating defect generation.[8]

Neither the imaginary part ($\chi''$) nor the real part ($\chi'$) of magnetic susceptibility show superconductivity for the undoped sample, expected to be non-superconducting. We call it “Ba122UR” with olive colored graph in FIG. 2.

Results of magnetic (FIG. 2) and electrical (FIGS. 3 & 4) measurements will now be discussed. FIG. 2 for the x = 5.7% crystal shows $T_c$ = 15.95 K from its $\chi''$ peak in the un-radiated (“2Ba5.7Co UR” in figure in wine colour) sample. After our Ar-irradiation of 2.5 × 10$^{15}$ ions/cm$^2$, this sample “5Ba5.7Co AR”, shows a surprising and significant increase of $T_c$ to $T_c$ = 24.01 K. Independent measurement of $T_c$ from electrical resistivity also records that 2.5 × 10$^{15}$Ar-ions/cm$^2$

In the present resistive transition, completion of the superconducting transition is being quoted as $T_c$. Onset superconducting transition temperature, real beginning of superconductivity, utilized in many publications, can be seen in our graphs to be much higher. Here, $T_c$ from completion of superconducting transition has been preferred, as it usually matches the $\chi''$ peak.

FIG. 3 shows (a) superconductivity-like sharp fall of electrical resistivity measured at different magnetic fields:0 to 6 Tesla directed along the c-axis of the single crystals of un-radiated BaFe$_2$As$_2$ (“Ba122 UR” sample, x = 0) on cooling from 21 K towards 10 K to a small non-zero value, a minimum; (b) detailed view of a slow semiconducting-type rise in resistivity of the same sample on cooling in the temperature range 10 to 2 K; and (c) 2.5×$10^{15}$Ar-ion/cm$^2$ irradiated $x = 0$ crystal (called 4Ba122 AR sample) shows sharp fall of resistivity to zero value with enhanced $T_c$ and no semiconductor-like rise of resistivity on further cooling to $T < T_c$.

Since FIG. 2(i) does not show $\chi''$ peak, bulk or sufficiently high bulk superconductivity can be concluded to be absent in Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$, x = 0 sample. The sharp resistive transition of FIG. 3(a) in this crystal is what is called spurious superconductivity or trace superconductivity. It has to be due to a somehow completed or almost completed superconducting path formed from possible superconducting impurity phase/s of such low volume fraction that detection by magnetic susceptibility failed (FIG. 2).

Present path can be assumed to be a case of “almost completed superconducting path” consisting of few long superconducting parts linked by semiconducting grains, to explain the semiconducting rise at lower temperatures. Above $T_c$, combined normal state resistance of the longer length superconducting paths must be high compared to that of the few semiconducting links so that the metallic character dominates. But below $T_c$, resistance of the semiconducting links is the only resistance so as to dominate and show the semiconducting rise of resistance on cooling in FIG. 3 (a) & (b) in the low temperature region (10 to 2 K).

A possible sources of above-mentioned superconducting (SC) impurity phases (providing SC paths) at crystal surface or domain boundaries in x = 0 sample can be growth of these SC phase/s due to inadvertent exposure to moisture, as in FeTe$_{0.6}Se_{0.2}$ powder.[9,10]. The physics of the water exposure causing superconductivity is not yet clarified. But, the surface of SrFe$_2$As$_2$ film, as discussed also by Katase et al. in 2009, shows growth of Fe$_2$As, a SC phase, after an exposure to water.[9,11]. Even this trace superconductivity appears to improve its $T_c$ in

Kriti R Shau et al.
FIG. 3(c) due to our 1.5 MeV Ar irradiation. Actually, our observed decrease of $T_c$ due magnetic field in Figs. 3 (a) & (c) should be taken as proof of real superconductivity, although it is non-bulk trace superconductivity.

Now, comes the detailed discussion (Fig. 4) of the bulk superconducting sample, Ba(Fe$_{0.943}$Co$_{0.057}$)$_2$As$_2$ single crystal HTSC, which responded positively in Fig. 2, to magnetic measurements. Fig. 4 shows superconducting transitions under 0, 1, and 6 T magnetic fields for Ba(Fe$_{0.943}$Co$_{0.057}$)$_2$As$_2$ crystals before (Fig. 4(a)) and after (Fig. 4(b)) 1.5 MeV Ar$^{+}$-irradiation. As expected, superconducting transition clearly shifts to lower temperatures on applying increasing magnetic fields, in un-irradiated as well as irradiated samples.

Surprising increase of the completion of transition of the 5.7% Co doped crystal due to Ar-irradiation has already been discussed. This resistively observed 8.2 K increase of $H = 0$ T superconducting transition temperature compare well with 8.06 K increase observed from magnetic susceptibility measurements. It is a significant discovery in view of widely reported irradiation damage or decrease of $T_c$ in Fe-HTSCs [12] and other superconductors due to energetic electron, ion, and neutron irradiation. Here, (i) Radiation-induced vanishing, in Fig. 3(c), of semiconductor-like rise of resistivity on cooling the $x = 0$ sample in 10 to 2 K range, (ii) no semiconductor-like rise of resistivity in $\sim$16 to 2 K range, on cooling the un-irradiated $x = 5.7\%$ sample (Fig. 4(a)) and (iii) return in the irradiated sample (i.e. in Fig. 4(b)) of much smaller but non-zero resistivity below $T_c$ and semiconductor-like rise of resistivity on further cooling, demand new explanation if these are internal phenomena in the sample. This issue will presently be left unsettled, as it does not affect the main investigation i.e. how $T_c$ is modified by the irradiation used.

Review of literature [13-15] showed that essentially the same irradiation dosage 1.8 C/cm$^2$ of 2.5 MeV electron beam produced (a) a suppression of 5% of $T_c$ in BaFe$_{2}$(As$_{0.7}$P$_{0.3}$)$_2$, (b) in contrast to an unusual $T_c$ increases by about the same amount in FeSe. Different mechanisms and effects in these two systems have, therefore, been believed to be at the root of the opposite effects in $T_c$. In fact, in above-mentioned FeSe (single crystals) the superconducting transition temperature $T_c$ increases by 0.4 K from $T_{c_0} = 8.8$ K, while the structural transition temperature $T_s$ decreases by 0.9 K from $T_{s_0} = 91.2$ K after the electron irradiation. After discussing several explanations for the $T_c$ enhancement, a local strengthening of the pair interaction by irradiation-induced Frenkel defects has been proposed as the most likely cause of $T_c$ increase. $T_c$ can be affected also by irradiation induced strain in the sample.

More literature survey for the rare cases of $T_c$ increase on fast ion and electron irradiation, follows, to illustrate conditions leading to such increase:

Sarlak et al [16] reported the enhancement and degradation of $T_c$ in Bi-HTSC due to Li$^+$-irradiations showed an increase of $T_c$ only in such Ba$_n$Sr$_{3-n}$CuO$_{6-y}$ (Bi-2212) samples that missed best $T_c$ due to our deliberately different chemical preparation. These samples had excess oxygen than is optimal. Removal of this excess oxygen from these samples by 50 MeV Li irradiation caused the increase of $T_c - \approx$ 0.3 K. Optimal $T_c$ in HTSC due to Li irradiation induced decrease of $T_c$ has been observed in the same work for samples having optimal O-content or less.

We reported earlier, an increase in critical temperature of over-doped Bi$_2$Sr$_2$CaCu$_2$O$_x$ superconductors due to alpha particle irradiation [17]. Our 13.6 MeV alpha irradiation of Nb$_5$Sn on Hastelloy (in a tape) in radiation damage studies of superconducting magnet materials as reported by De et al. in 1984 [18] showed small increase in $T_c$ only at low dose, with expected decrease at higher doses. We conjecture that the initial increase of $T_c$ must have been due to removal of mechanical strain in the Nb$_5$Sn layer, CVD-deposited on the metallic substrate. Mizukami et al. [19], reported in 2017 that for BaFe$_2$As$_2$ with $x = 0.16$ & 0.24, a final reduction of the temperature of the onset of superconductivity (here called $T_c$ upon the introduction of disorder by an electron beam with an incident energy of 2.5 MeV. Authors found $T_c$ to gradually increase (by up to 2 K) with increasing radiation dose up to $\approx 3 C/cm^2$. Although the resistivity did not reach zero for $x = 0.16$, the initial increase of $T_c$ is clear for both $x = 0.16$ and 0.24. Then, $T_c$ decreased at higher doses. That means, although the superconducting transition temperature $T_c$ is depressed at $x$ = 0.057, it increases by about the same amount in FeSe. Different mechanisms and effects in these two systems have, therefore, been believed to be at the root of the opposite effects in $T_c$. In fact, in above-mentioned FeSe (single crystals) the superconducting transition temperature $T_c$ increases by 0.4 K from $T_{c_0} = 8.8$ K, while the structural transition temperature $T_s$ decreases by 0.9 K from $T_{s_0} = 91.2$ K after the electron irradiation. After discussing several explanations for the $T_c$ enhancement, a local strengthening of the pair interaction by irradiation-induced Frenkel defects has been proposed as the most likely cause of $T_c$ increase. $T_c$ can be affected also by irradiation induced strain in the sample. 

Kriti R Shau et al.,

International Journal of Advanced Science and Engineering www.mahendrapublications.com
FIG. 3. Temperature dependence of electrical resistivity at different magnetic fields of 0, 1, and 6 Tesla applied along the c-axis for single crystals of (a) un-radiated BaFe\(_2\)As\(_2\) (called “Ba122 UR”) in the temperature range 21 to 10 K; (b) un-radiated BaFe\(_2\)As\(_2\) (called “Ba122 UR” sample) in the temperature range 10 to 2 K, where resistance decreases with temperature showing a semiconducting nature; and (c) 2.5 × 10\(^{15}\) cm\(^{-2}\) Ar-radiated BaFe\(_2\)As\(_2\) (called “4Ba122 AR” sample) in the temperature range 26 to 2 K.

FIG. 4. Temperature dependence of electrical resistivity at different magnetic fields of 0, 1 and 6 Tesla) applied along c-axis for single crystals of (a) un-radiated 5.7% Co doped BaFe\(_2\)As\(_2\) (“Ba5.7Co UR”) in temperature range 25.5 to 2 K, showing superconducting transition, (b) 2.5 × 10\(^{15}\) Ar-ion/cm\(^2\) irradiated 5.7% Co-doped BaFe\(_2\)As\(_2\) (“5Ba5.7Co AR”) in the temperature range 25 to 15 K.

Kriti R Shau et al.,

International Journal of Advanced Science and Engineering www.mahendrapublications.com
4. CONCLUSION
All characterizations detect radiation induced changes in these Ba(Fe\textsubscript{1-x}Co\textsubscript{x})\textsubscript{2}As\textsubscript{2} Single Crystal samples due to 1.5 MeV (entering energy) Ar\textsuperscript{+} beam. We observe T\textsubscript{c} increase on 1.5 MeV Ar irradiation, but with broadened superconducting transition. Single Crystal samples with x = 5.7% Co show convincing T\textsubscript{c} ince of ~ 8 K from electrical as well as magnetic measurements.

ACKNOWLEDGEMENTS
We thank IUAC, New Delhi, for granting us a project (Ref: IUAC/XIII.3A/ 2ndAugust 2016 with BTR No. 60526). We thank UGC-DAE Consortium for Scientific Research, Indore Centre, India, for funding the research stay for one of us (KRS) to take a few measurements. It is a pleasure to acknowledge the help of IUAC, New Delhi, colleagues P K Kuriya, S Ojha, F Singh, S A Khan and D Kanjilal for facilities like Ar irradiation and XRD. One of the authors (UD) thanks Alexander von Humboldt Foundation, Germany, for partially supporting KIT collaboration and participation in a conference in Berlin.

REFERENCES

[5] Sanyal, D., Wolf, T., Chakrabarti, M., De, U., 2014. Positron probing of electron momentum re-distribution at the superconducting transition in Ba(Fe\textsubscript{1-x}Co\textsubscript{x})\textsubscript{2}As\textsubscript{2} single crystals. Solid State Communications, 180, 35-38.
[10] Mizuguchi, Y., Deguchi, K., Tsuda, S., Yamaguchi, T., Takano, Y., 2010. Moisture-induced superconductivity in FeTe\textsubscript{0.9}Se\textsubscript{0.1}. Physical Review B, 81, 214510-1-214510-5.
Superconducting Phase Diagram in BaFe$_2$(As$_{1-x}$P$_x$)$_2$. Journal of the Physical Society of Japan, 86, 083706-1-083706-4.