

This is the accepted manuscript made available via CHORUS. The article has been published as:

## Suppression of superconductivity in Fe chalcogenides by annealing: A reverse effect to pressure

Despina Louca, Jiaqiang Yan, Anna Llobet, and Ryotaro Arita

Phys. Rev. B **84**, 054522 — Published 10 August 2011

DOI: [10.1103/PhysRevB.84.054522](https://doi.org/10.1103/PhysRevB.84.054522)

# Suppression of superconductivity in Fe chalcogenides by annealing: a reverse effect to pressure

Despina Louca,<sup>1</sup> Jiaqiang Yan<sup>#,2</sup>, Anna Llobet,<sup>3</sup> and Ryotaro Arita<sup>4</sup>

<sup>1</sup>*University of Virginia, Department of Physics, VA 22904, USA*

<sup>2</sup>*Ames Laboratory, Iowa State University, Ames, IA 50011, USA*

<sup>3</sup>*Lujan Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.*

<sup>4</sup>*Department of Applied Physics, University of Tokyo, and JST TRIP, Tokyo 113-8656, JAPAN*

Superconductivity in  $\text{FeTe}_{1-x}\text{Se}_x$  can be controlled by annealing, in the absence of extrinsic influences. Using neutron diffraction, we show that  $T_C$  sensitively depends on the atomic configurations of the Te and Se ions. Low temperature annealing not only homogenizes the Te and Se ion distribution, it suppresses  $T_C$  because of changes in the chalcogen ions' z-parameter. In particular, the height of Te from the Fe basal plane is much reduced while that for Se shows a modest increase. These trends are reverse of the effects induced by pressure.

PACS numbers: 61.05.F-, 74.62.Dh, 74.70.Ad, 75.50.Bb

Extensive experimental and theoretical works on the iron pnictides and chalcogenides have revealed important traits of these itinerant magnets [1–3]. In particular, their Fermi surface topologies are remarkably similar except for the recently discovered  $\text{A}_x\text{Fe}_2\text{Se}_2$  (A-alkali element) system, and both classes exhibit a superconducting spin resonance around  $(\pi, \pi)$  [4–6]. While the origin of the pairing mechanism is still under debate [7, 8], it is nonetheless clear that the proximity of magnetism to superconductivity is crucial in the Fe pnictides as it is in the cuprate superconductors. A common route to controlling the superconducting transition temperature ( $T_C$ ) is to introduce charge carriers via chemical substitution or to apply pressure [9–11]. The emergence of superconductivity with the addition of charge carriers in the antiferromagnetically ordered parent compounds of the  $\text{LaFeAsO}$  (1111) or  $\text{BaFe}_2\text{As}_2$  (122) ferro-pnictide families resembles the physics of the copper oxides although the ground state of the latter is insulating while the former are metallic[8]. In both pnictide families, the orthorhombic and magnetically ordered parent phase is suppressed with the onset of superconductivity in the tetragonal phase. The transition is accompanied by an optimization of important structural components, reflected in the As-Fe-As bond angle, the As height from the Fe plane (the z-parameter) and the Fe-Fe bond length[12, 13]. These components exhibit a similar dependence to pressure as with doping in both the pnictides as well as in the chalcogenides[10, 14–18]. In the pnictides it was shown that the anion height and the tetrahedral bond angle reach optimal values, 1.38 Å and  $\sim 109^\circ$  respectively, on approaching the maximum  $T_C$ [12, 13]. Remarkably, very little is known of the mechanism that suppresses  $T_C$  and of the changes brought upon the electronic structure, as is the case of overdoping in 122 [19], or impurity doping in 1111 [20].

Carrier doping is not vital for superconductivity however, and here we focus on the binary  $\text{FeTe}_{1-x}\text{Se}_x$  where the chemical pressure induced by the isovalent substitu-

tion of half of the Se sites with Te is sufficient to nearly double  $T_C$  at this optimal concentration. The transition temperature shows a dramatic increase under hydrostatic pressures [16]. Yet, pressures in excess of 2 GPa [17] lead to leveling off and subsequent reduction of  $T_C$ . This parallels the behavior observed in the pnictides in which the adverse effect overdoping has on  $T_C$  gives rise to the superconducting dome, for reasons that are not clearly understood at present. In the Ba-122, there is no apparent structural signature linked to the reduction of  $T_C$  above a Co doping in excess of  $x \sim 0.12$ [18]. Whether or not the suppression of  $T_C$  is the result of introducing many defects or impurities that change the Fermi surface remains an open question. Resolving this challenging issue is not only relevant to understanding impurity effects but has an impact on our understanding of superconductivity in this class of materials.

To address this issue, we investigated through transport, magnetization and neutron diffraction, how the crystal structure and properties change by annealing  $\text{FeTe}_x\text{Se}_{1-x}$ , without introducing foreign atoms or applying pressure. Three compositions close to the optimal concentration yielding the highest  $T_C$  ( $x \sim 0.5$ ) were looked at. Annealing is generally thought to improve sample quality, recently reported in three crystal systems,  $\text{Sr}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [21],  $\text{Sr}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ [22] and  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [23]: by reducing the amount of sample inhomogeneities through annealing, it was observed that the magnetic or superconducting transition temperatures improved. In the Ba-122 with Co for instance, annealing increases  $T_C$  and reduces the residual linear term of the specific heat presumably due to the reduction of sample inhomogeneities[23]. By comparison, in the Ce electron doped cuprate superconductors,  $T_C$  is very sensitive to the annealing temperature and partial pressure of oxygen[24], and superconductivity is observed only after annealing the samples in a reducing atmosphere that introduces oxygen vacancies. Thus annealing tends to increase  $T_C$  typically through effective doping by either

changing the stoichiometry or improving sample homogeneity.

Annealing  $\text{FeTe}_x\text{Se}_{1-x}$  however has a surprisingly opposite effect. Three polycrystalline pellets with the starting nominal compositions of  $x \sim 0.48, 0.50$ , and  $0.52$  were synthesized by solid state reaction method. The starting materials of Fe (99.99%), Se (99.9%) and Te (99.9%) were mixed in stoichiometric amounts, pelletized, and sealed in an evacuated quartz tube backed filled with 1/3 atmosphere of argon. The ampoules were then fired at  $680^\circ\text{C}$  for 4 days. Half of the pellets were then resealed in an evacuated quartz tube and further annealed at  $550^\circ\text{C}$  for additional four weeks. Long time annealing may cause compositional fluctuations as reported in Ref. [25] but no weight loss was observed. The mass change was carefully monitored before and after the annealing process and no observable mass loss was observed. Elemental analysis was performed by WDS on polished surfaces before and after annealing. In the as grown  $\text{FeSe}_{0.5}\text{Te}_{0.5}$ , the majority phase tends to be Te-rich with an atomic ratio of Fe:Te:Se = 50.2:27.3:22.5 after the initial synthesis at  $680^\circ\text{C}$ . The most prominent minority phase is  $\text{Fe}_5\text{Se}_2\text{Te}_5$ , with a volume fraction of about 6 %. However, after long time annealing, a thermal redistribution of Se and Te ions occurs and the majority phase gets quite close to the nominal composition with the atomic ratio of Fe:Te:Se = 49.9:24.4:25.7. Fewer impurity phases are observed in the annealed samples, the same observation made in another composition,  $\text{FeSe}_{0.39}\text{Te}_{0.61}$  by [25], emphasizing that low temperature annealing prevents phase separation in contradiction to what has been reported on high temperature single crystal synthesis [26]. The growth of high quality  $\text{FeSe}_{1-x}\text{Te}_x$  single crystals is still problematic, most likely having to do with the high temperature synthesis. Most as-grown single crystals are nonsuperconducting above 2 K [26]. The reason for this is not quite understood yet. The higher temperatures required to prepare single crystals tend to promote phase separation, leading to poor superconducting properties. However, at present, superconducting  $\text{FeSe}_{1-x}\text{Te}_x$  polycrystalline samples can be synthesized reproducibly by conventional solid state reaction technique. Our annealing procedure at low temperatures has shown, in agreement with [25, 27], that a single phase can be achieved and a greater ion distribution leads to better superconducting properties.

Although the  $x \sim 0.5$  compositions show bulk superconductivity before and after annealing, the optimization of the Se/Te distribution has a profound effect on the physical properties.  $T_C$  of the annealed samples is reduced by  $\sim 2$  K, a 15 % change. This reduction in  $T_C$  was observed in all three compositions studied. Shown in Fig. 1(a) is the temperature dependence of the resistance of the  $x \sim 0.5$  and  $0.52$  samples before and after annealing, normalized to the resistance at room temperature. Before annealing, the systematic substitution

showed a consistent dependence of  $T_C$  with Se content, and the values are in agreement with published data on this system[5, 16]. The resistance plot shown in (a) is indication that annealing has an adverse effect on superconductivity; namely  $T_C$  is suppressed. Although grain coarsening occurs after annealing as observed by SEM, it will not suppress  $T_C$ . The same observation was made from the bulk susceptibility data. Specifically the diamagnetic susceptibility of Fig. 1(b) shows a reduction of  $T_C$  with annealing which is in stark contrast to the reported effects of annealing in the 122 series and in the cuprate family. Can the homogenization account for the suppression of  $T_C$ ? Based on the elemental analysis with WDS, the change cannot be responsible for the suppression of  $T_C$  because (1)  $T_C$  should increase as the composition moves toward the nominal  $\text{FeSe}_{0.5}\text{Te}_{0.5}$ , and (2) a two degree drop around  $x = 0.50$  requires a change in  $x$  of about 20 % according to the phase diagram showing the evolution of  $T_C$  with  $x$  in  $\text{FeSe}_{1-x}\text{Te}_x$ [5]. Grain boundaries might affect the physical properties as well. Generally, the transition, the superconducting transition in the current case, would be broadened due to grain boundary scattering. We carefully compared the superconducting transition of our samples and the transition width is comparable before and after annealing as seen in Fig. 1a and 1b. The suppression of  $T_C$  is obviously not due to the grain boundary effect.

To understand the origin of the reduction in  $T_C$ , we looked at the electronic and crystal structures in detail. Neutron diffraction data were collected at HIPD of Los Alamos National Laboratory above and below  $T_C$  for all compositions, and shown in Fig. 1(c) are the diffractograms for the  $x = 0.5$  sample before and after annealing. The data were normalized by a vanadium standard and each spectrum was further normalized by using the integrated area under the  $3.2 \text{ \AA}^{-1}$  peak. Also shown in the figure is the difference between the two patterns which indicates that although no new peaks are observed after annealing, the peaks shift with annealing. The crystal structure shown in Fig. 1(d) is tetragonal at all temperatures. If excess Fe at the  $2c$  site is introduced, the refinement yields negligible occupancy. The data were analyzed using two symmetries, the  $P4/nmm$ , which is the symmetry typically used for these crystal systems, and the  $P4mm$ . Both symmetries are tetragonal but the  $P4mm$  allows for two unique sites of the chalcogen ions. The latter symmetry can best describe the local arrangement of the Te and Se ions determined earlier from a local structure analysis [28]. Although no long-range ordering of the Se and Te ions takes place, concurred by the absence of superlattice peaks, they are nevertheless not sharing the same site as they give rise to distinct local bonds with Fe that serve as strong indication that Se and Te occupy unique sites in the lattice, albeit randomly. Both crystal symmetries can fit the diffraction data and the refinement results are comparable, although

the  $P4/nmm$  symmetry consistently yields larger thermal factors. A total of six samples were measured. As we increase the Se doping from 0.48 to 0.52, the pattern shifts to the left as expected because the Se ion is smaller than the Te ion and the lattice constants are reduced. The unit cell volume decreases as shown in Fig. 2. If compared to the value before annealing, it is clear that annealing has the effect of reducing the volume because of a lattice contraction. Both  $c$ - and  $a$ -lattice constants decrease and so does the  $c/a$  ratio shown in the inset of this figure consistently for the three values of  $x$ . The lattice contraction is about 0.5 % along the  $c$ -axis for the  $x = 0.5$  composition after annealing, which corresponds to  $\sim 0.03$  Å change with annealing. Such a lattice contraction is most likely in response to the ion homogenization, where after annealing, less Te is in the majority phase as mentioned earlier. However, from the structure analysis, we can also deduce that the  $z$ -parameters for the Se and Te change, especially for Te (shown in the inset). At  $x = 0.5$ , the height of the Te ion from the basal plane is reduced by 0.04 Å, and is the dominant effect, while for Se the change is smaller,  $\sim 0.002$  Å. The reduction in the Te  $z$ -parameter is not simply from the lattice contraction, however, as it follows the opposite trend to the volume. Also from Fig. 2, the as-prepared  $\text{FeSe}_{0.5}\text{Te}_{0.5}$  and annealed  $\text{FeSe}_{0.48}\text{Te}_{0.52}$  have the same unit cell volumes but different Te  $z$ -parameters, indicating that the change in Te height is not simply from the redistribution of Te.

The structural changes brought upon by annealing are markedly different from the effects induced under pressure. A comparison of the tetrahedral units of the crystal (a) before annealing, (b) after annealing and (c) under pressure is shown in Fig. 3. In (c), the structural parameters were obtained from the authors of Ref. [16]. Pressure, in addition to changing the volume by a significant amount, changes the Se  $z$ -parameter or anion height significantly while annealing mainly changes the Te  $z$ -parameter. The Te height decreases by 0.04 Å after annealing while the Se height decreases by 0.04 Å under pressure. With annealing, the bond length between Te and Fe decreases while simultaneously, the bond angle between them increases compared to the values before annealing. On the other hand, the bond length between Se and Fe decreases but the bond angle between them is reduced and the Se height increases. Under pressure however, the Se height decreases while the angle approaches the optimal  $109^\circ$  as seen in (c). The reverse is true for Te, namely its height increases while the bond angle is reduced under pressure.

The electronic band structure and partial density of states were calculated using the structural parameters determined under three different conditions and results are shown in Fig. 4. The WIEN2k[29] package with the generalized-gradient-approximation (GGA) exchange correlation functional[30] were used. The band structure

shown in (a) corresponds to the crystal structure before annealing while that in (b) corresponds to the crystal structure after annealing. The change in the electronic structure between (a) and (b) is negligibly small and difficult to see. This suggests that the factors that control  $T_C$  under annealing cannot be detected by the standard LDA electronic structure calculations. On the other hand, in (c), the band structure under pressure clearly shows an increase in the bandwidth compared to the one in (a). This change mostly comes about because of the volume change, which is quite dramatic under pressure ( $\sim 8\%$ ). At the same time, since the volume change under annealing is quite small by comparison, the band structure changes are hardly noticeable.

Previous studies on the Fe-based superconductors have focused on the effects of the  $z$ -parameter early on. However, no study has been performed on a single composition to monitor the evolution of the physical properties while changing the  $z$ -parameters, without introducing foreign atoms or applying pressure. All studies have focused on different compositions. In our study, we annealed to homogenize the sample without any external influences. As stated above, the small compositional fluctuation resulting from the homogenization should raise  $T_C$  according to the well developed phase diagrams. But this is not what is happening. The change of the Se ion coordinates (i.e. height and angle) is small, while the change of the Te ion coordinates is large and is the dominant factor that changes the physical properties. Our results clearly demonstrate the effect of the Te-height on the properties.

What is the origin of the reduction of  $T_C$  with annealing in the 11 family? It is clear that in the 11 family, there are many possible factors which determine  $T_C$ . In this regard, several theoretical proposals have been made. For example, if we assume that the superconductivity is mediated by spin fluctuations caused by Fermi-surface nesting, how the Fermi-surface changes by controlling the  $z$ -parameter is important[31]. Local spin-density approximation studies suggested that superconductivity should be enhanced when Te is further from the Fe plane. The decreased Te  $z$ -parameter and ensuing suppression of  $T_C$  reported in this paper suggests that the pairing is mediated by spin fluctuations [32]. On the other hand, it has also been claimed that the  $z$ -parameter dependence is an indication of the importance of orbital fluctuation in this system [33]. In this study we have shown how the local atomic configuration of the chalcogen ions and in particular the height of Te is the dominant factor suppressing  $T_C$ . This change is not realized by applying external pressure or introducing foreign atoms in the lattice.

The authors would like to thank K. Horigane for providing high pressure data on the  $\text{FeTe}_{1-x}\text{Se}_x$  system for comparison, and W. E. Straszheim for his help in the elemental analysis. This work is supported by the U. S. Department of Energy, Office of Basic Energy Sci-

ences under contract DE-FG02-01ER45927, DE-AC02-07CH11358 and Division of Scientific User Facilities under contract DE-AC52-06NA25396.

<sup>#</sup>Current address: Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA.

- 
- [1] D. J. Singh, M.-H. Du. Phys. Rev. Lett. **100**, 237003 (2008).
  - [2] I. I. Mazin *et al.*, Phys. Rev. Lett. **101**, 057003 (2008).
  - [3] A. Subedi *et al.*, Phys. Rev. B **78**, 134514 (2008).
  - [4] A. D. Christianson *et al.*, Nature **456**, 930 (2008).
  - [5] T. J. Liu *et al.*, Nature Mater. **9**, 718 (2010).
  - [6] Y. M. Qiu *et al.*, Phys. Rev. Lett. **103**, 067008 (2009).
  - [7] A. V. Chubukov *et al.*, Phys. Rev. B **80**, 140515(R) (2009).
  - [8] T. Yildirim. Physica C **469**, 425 (2009).
  - [9] Y. Kamihara *et al.*, J. Am. Chem. Soc. **130**, 3296 (2008).
  - [10] S. A. J. Kimber *et al.*, Nature Mater. **8**, 471 (2009).
  - [11] M. Rotter, M. Tegel, and D. Johrendt. Phys. Rev. Lett. **101**, 107006 (2008).
  - [12] C.-H. Lee *et al.*, J. Phys. Soc. Jpn. **77**, 083704 (2008).
  - [13] Y. Mizuguchi and Y. Takano. arXiv: 1003.2696.
  - [14] V. A. Sidorov *et al.*, J. Phys.: Cond. Mat. **21**, 415701 (2009).
  - [15] T. Imai *et al.*, Phys. Rev Lett. **102**, 177005 (2009).
  - [16] K. Horigane *et al.*, J. Phys. Soc. Jpn. **78**, 063705 (2009). The authors provided us atomic parameters under pressure analyzed in the  $P4mm$  symmetry for comparison. Their ambient pressure data were normalized to our as-grown data to compensate for the differences in instruments used for data collection.
  - [17] A. Kreyssig *et al.*, Phys. Rev. B **78**, 184517 (2008).
  - [18] A. S. Sefat *et al.*, Phys. Rev. Lett. **101**, 117004 (2008).
  - [19] S. Sharma *et al.*, Phys. Rev B **81**, 174512 (2010).
  - [20] Y. F. Guo *et al.*, Phys. Rev. B **82**, 054506 (2010).
  - [21] J. Gillett *et al.* arXiv:1005.1330v1.
  - [22] S. R. Saha *et al.*, Physica C: Superconductivity **470**, S379 (2009).
  - [23] K. Gofryk *et al.*, arXiv:1009.1091v1
  - [24] H. Takagi, S. Uchida and Y. Tokura. Phys. Rev. Lett. **62**, 1197 (1989).
  - [25] T. Taen, Y. Tsuchiya, Y. Nakajima, and T. Tamegai, Phys. Rev. B **80**, 092502 (2009).
  - [26] B. C. Sales *et al.*, Phys. Rev. B **79**, 094521 (2009).
  - [27] T. Noji, T. Suzuki, H. Abe, T. Adachi, M. Kato, and Y.

Koike, arXiv:1004.1038

- [28] D. Louca *et al.*, Phys. Rev. B **81**, 134524 (2010).
- [29] K. Schwarz. Solid State Commun. **176**, 319 (2003).
- [30] J. P. Perdew *et al.*, Phys. Rev. Lett. **77**, 3865 (1996).
- [31] K. Kuroki *et al.*, Phys. Rev. B **79**, 224511 (2009).
- [32] L. Zhang *et al.*, Phys. Rev. B **78**, 174520 (2008).
- [33] T. Saito *et al.*, Phys. Rev. B **82**, 144510 (2010).

Figure captions:

Figure 1: (a) A plot of the resistance normalized to the room temperature value for two of the samples, the  $x = 0.5$  and 0.52. A reduction in  $T_C$  is observed for both samples. (b) The  $M/H$  curve for the annealed and as prepared sample of  $x = 0.5$  sample shows the same transitions as the resistance plot. (c) The diffraction patterns compared before and after annealing in the  $x = 0.5$  composition. The peaks become sharper and shift to the left after annealing. d) The crystal structure shown with the Se and Te sharing the same site.

Figure 2: a) The effect of annealing on the unit cell volume at the three compositions. The  $c/a$  ratio is shown in the inset. Also shown are the  $z$ -parameters for Te and Se before and after annealing. The error bars are smaller than the actual points shown.

Figure 3: The bond angles, bond lengths and Te and Se ions height from the basal plane are compared in the crystal structures (a) before annealing, (b) after annealing and (c) under pressure. The parameters at 0 pressure obtained from Ref. [16] were normalized to our results before annealing in order to calibrate the values of the parameters considering that they were obtained using two different instruments. The height of the Te ion changes dramatically with annealing but less so under pressure. The reverse happens with Se.

Figure 4: The band structure corresponding to the crystal of  $\text{FeSe}_{0.5}\text{Te}_{0.5}$  a) before annealing, b) after annealing and c) at 2 GPa. The band width expands in the range of -2 to +2 eV quite drastically under pressure when the volume changes from 85.683  $\text{\AA}^3$  to 79.652  $\text{\AA}^3$ , and the Se height decreases from 1.4581 to 1.4162  $\text{\AA}$ . However, the band width contracts by a small amount under annealing in the same energy region when the volume changes from 85.683  $\text{\AA}^3$  to 85.073  $\text{\AA}^3$  and the Se height increases from 1.4581 to 1.4596  $\text{\AA}$ .



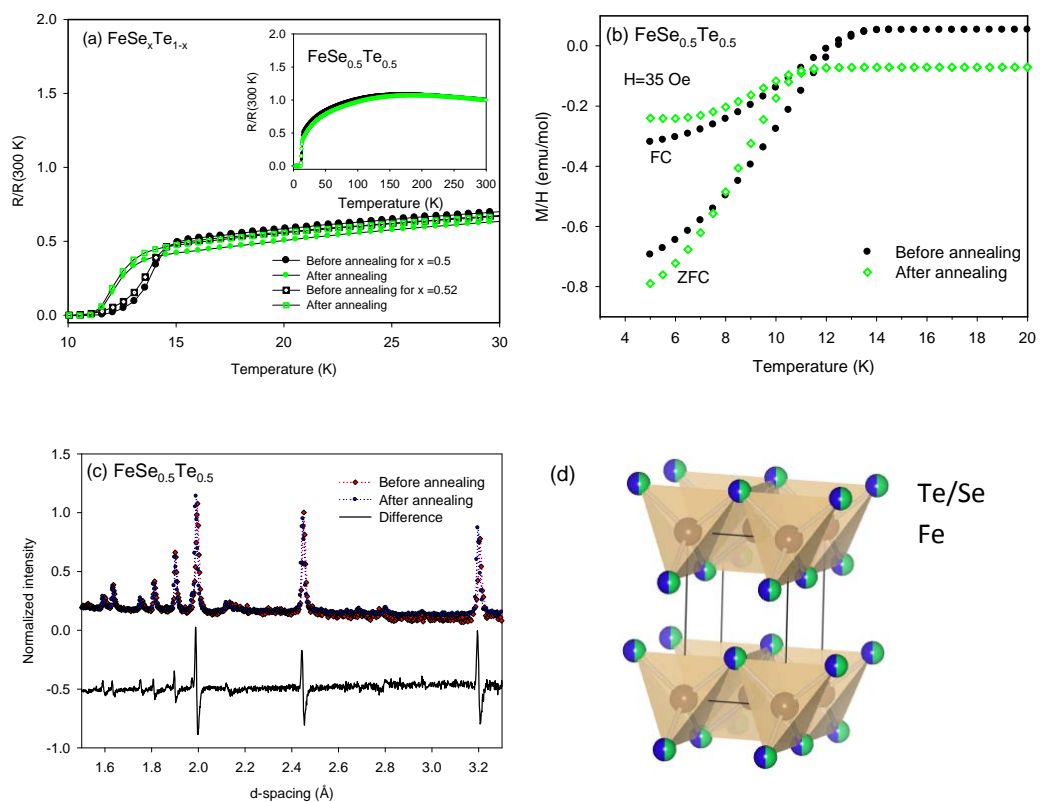
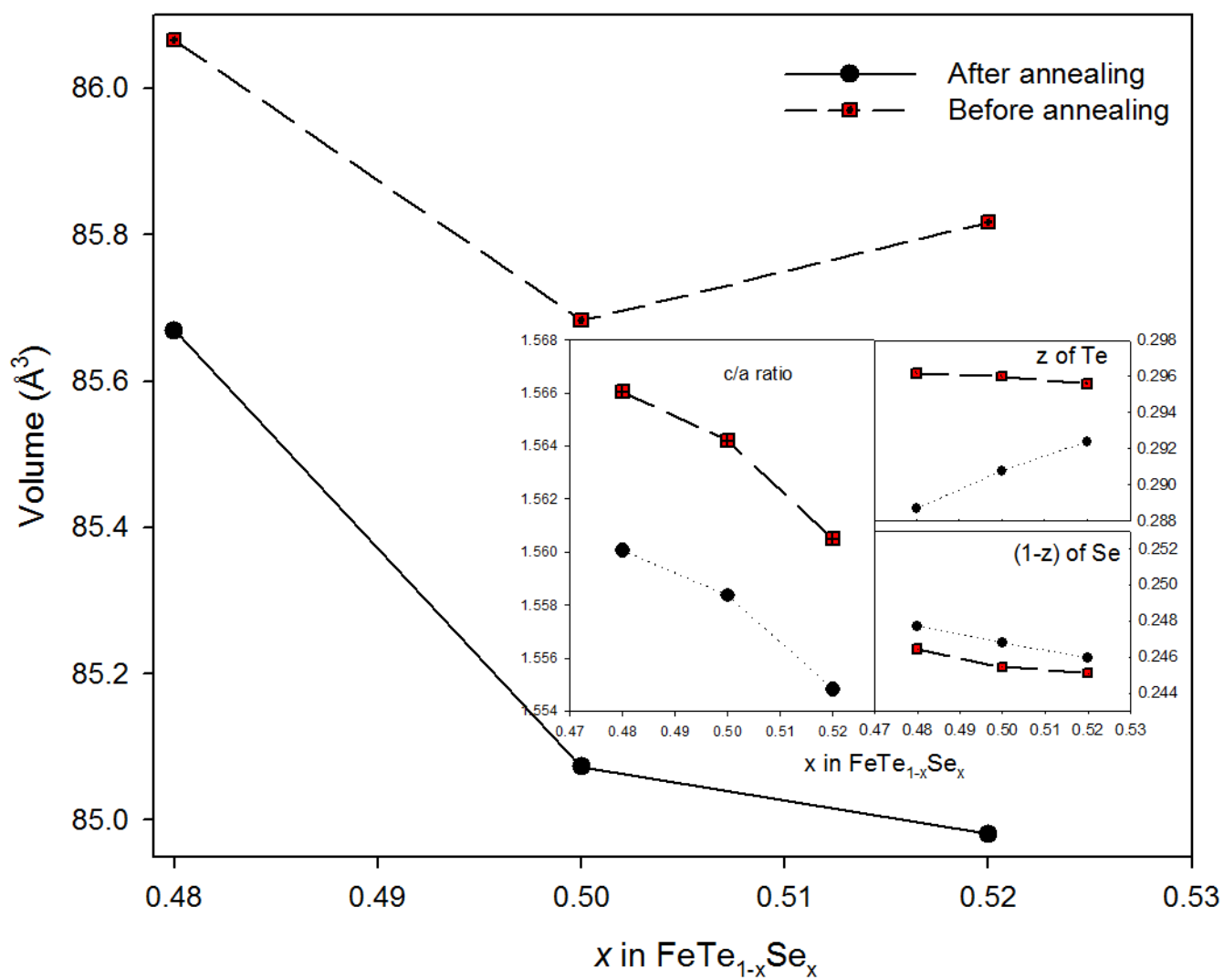
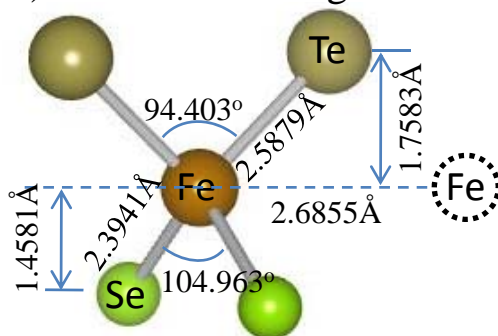


Fig. 1, Louca et al.

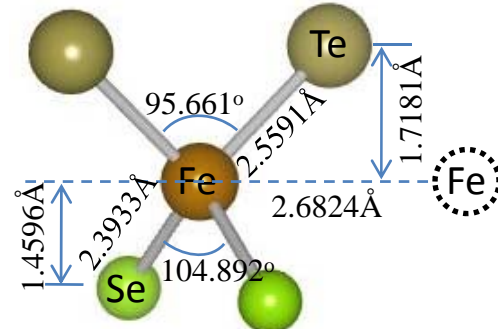


Louca et al., Fig. 2

a) Before annealing



b) After annealing



c) Under pressure

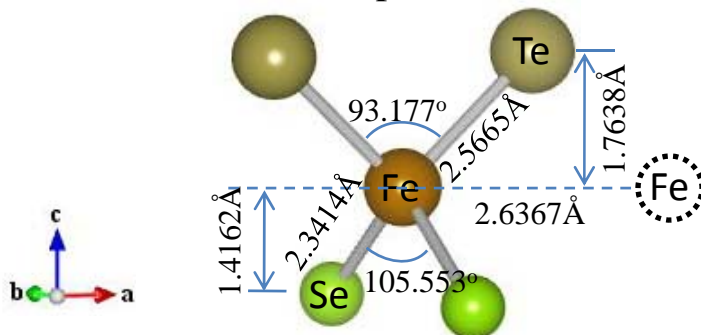


Fig. 3, Louca et al.



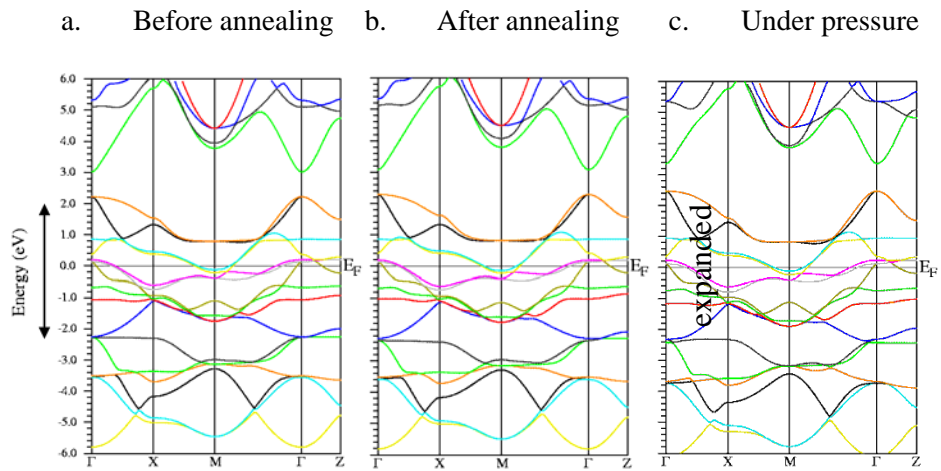


Fig. 4, Louca et al.