Mössbauer studies of powdered single crystals of FeTe$_{0.5}$Se$_{0.5}$

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Abstract

Mössbauer measurements performed on powdered single crystals of FeTe$_{0.5}$Se$_{0.5}$ ($T_c \sim 14.7$ K) reveal minor content of two impurity phases, identified as Fe$_3$O$_4$ and Fe$_7$Se$_8$, among the major tetragonal phase. From the shape of the impurity subspectra it follows that Fe$_7$Se$_8$ behaves in a superparamagnetic manner, most likely because of randomly distributed Fe vacancies in the lattice structure of Fe–Te–Se. The magnetite content in the powdered absorber exposed to ambient air conditions remains unchanged during a period of 16 months. Ageing effects are observed for the samples stored under argon atmosphere and a small increase of the isomer shift of the doublet is detected. The presented temperature dependence of the hyperfine parameters can be explained as due to possible orthorhombic distortion or to temperature behaviour of the impurity phases Fe$_3$O$_4$ and Fe$_7$Se$_8$. A strong tendency for the formation of crystalline texture of the powdered sample is observed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Very soon after the discovery of superconductivity in LaFeAsO$_{1-x}$F$_x$ pnictides with $T_c \sim 26$ K [1], superconductivity was found in the chalcogen–iron system FeSe$_{1-x}$ ({$T_c \sim 8.5$ K}) [2] with the simple chemical formula and the same layered tetrahedral crystalline motif. McQueen et al [3] reported a very narrow range of the $\delta$ value, $\delta = 0.01$–0.03, in which the material shows superconductivity. Williams et al [4] confirmed that only FeSe$_{0.99}$ contains the tetragonal phase without iron precipitation as well as without the presence of an additional Fe$_7$Se$_8$ phase. These reports indicate the extreme sensitivity of the superconductivity in the Fe–Se system to the appearance of any defects in the crystal structure and of any impurities, such as Fe$_3$O$_4$ or Fe$_7$Se$_8$.

Various chemical substitutions to the Fe–Se system were made. It was found that substitution of a part of the selenium by tellurium leads to the isostructural, pseudobinary system of Fe–Te–Se with higher $T_c$ up to $15$ K [5, 6]. In many reports on the Fe–Te–Se system, the authors have noticed a magnetic anomaly at about 120 K [7, 8], seen in electrical [9] or thermal [8, 10] transport measurements. Very often the anomaly was linked to the Verwey transition [11] in Fe$_3$O$_4$ [8]. Moreover, impurities of Fe$_7$Se$_8$ were detected in structural [12] and Mössbauer measurements [7]. However, it was concluded that impurities whose content does not extend beyond 3% do not affect the superconducting properties of the Fe–Te–Se system, in contrast to the impact of such phases on the superconductivity in the Fe–Se system. On the other hand, in reports describing substitution of Fe by Co, Ni and Cu ions, strong suppression of superconductivity in both the Fe–Se and Fe–Te–Se systems was noticed even with a substitution as small as 1–2% [13, 14].

In order to better understand the local structure of the Fe–Te–Se system and the role of the impurities and defects in the formation of the superconducting state we performed Mössbauer studies of powdered single crystals of FeTe$_{0.5}$Se$_{0.5}$. The Mössbauer technique is sensitive to the hyperfine magnetic field sensed by the $^{57}$Fe probe and thus the coexistence of magnetic ordering and superconductivity could be investigated. This type of study demonstrates the suppression of magnetic ordering by substitution of a part of the oxygen by fluorine.
Figure 1. The Mössbauer spectra of the FeTe$_{0.5}$Se$_{0.5}$ with a planar density 21(1) mg cm$^{-2}$: (a) for freshly prepared absorber, and for the absorber exposed to air for (b) 19 days, (c) 4 months, (d) 6 months, (e) 16 months. (f) The same absorber measured together with an extra 3.6 mg cm$^{-2}$ of Fe$_3$O$_4$.

Figure 2. Influence of grinding on the content of minority magnetic phases in the studied materials. Magnetization hysteresis loops of FeTe$_{0.5}$Se$_{0.5}$ single crystal and powder obtained by grinding under argon and in air at ambient conditions. The data were recorded at 20 K in magnetic fields of $-6$ to $+6$ kOe.

in LaFeAsO [15] and a spin wave anomaly in BaFe$_2$As$_2$ [16]. On the other hand, measurements of the recoilless fraction reveal anomalies in the iron dynamics recently observed in LiFeAs [17] and FeTe$_{0.5}$Se$_{0.5}$ [7].

2. Experimental details

Superconducting single crystals of FeTe$_{0.5}$Se$_{0.5}$ were grown using Bridgman’s method. The samples were prepared from stoichiometric quantities of iron chips (3N5), tellurium powder (4N) and selenium powder (pure). A double-walled evacuated sealed quartz ampoule containing the starting materials was placed in a furnace with a vertical temperature gradient. The samples were synthesized for 6 h at 680 °C, then the temperature was increased up to 920 °C. After melting, the temperature was held for 3 h, then the samples were cooled down to 400 °C at a rate of 3 °C h$^{-1}$ and next to 200 °C at a rate of 60 °C h$^{-1}$, and finally cooled down to room temperature with the furnace. The obtained crystals exhibited a natural cleavage plane (001). They were superconducting and exhibited a sharp transition to the superconducting state with a critical temperature about $T_c \sim 14.7$ K. Details about the superconducting properties, structural and chemical analysis of the grown crystals have been published elsewhere [18].

Bulk pieces of FeTe$_{0.5}$Se$_{0.5}$ compound were manually ground to a powder under argon atmosphere in a glove box. We checked that grinding (at room temperature) did not affect $T_c$. Absorbers for the Mössbauer measurements were prepared by distributing the powder on a Scotch Tape. The planar mass density of the powder was measured. A standard spectrometer working in the constant acceleration mode, equipped with a closed-cycle refrigerator, was used for the Mössbauer measurements. The lowest temperature available in our experimental setup was 13.3 K. During these measurements the absorbers were kept inside an evacuated cryostat in order to protect the samples from oxidation. In order to determine whether the samples exhibited any oxidation effect, some of the absorbers were exposed to air and measured systematically at various times since exposition, see figure 1. Clear-cut evidence of the presence of a small amount of magnetite follows from the observed spectra when one compares the spectrum of a 16 months old sample with the spectrum of a sample with an intentionally added minute quantity of magnetite (figures 1(e) and (f)). In order to observe ageing of the samples, the remaining part of freshly prepared powder was stored under argon atmosphere and after 13 months new absorbers were prepared for the second series of Mössbauer experiments. This part of the experiment was carried out using a new source with larger activity.

In order to demonstrate to what extent mechanical grinding introduces additional phases to the parent compound and therefore influences the content of minority phases in the studied materials, magnetization measurements were performed at a temperature above the transition temperature to the superconducting state on a piece of single crystal, on fresh powder obtained by grinding under argon atmosphere and on powder obtained by grinding in air at ambient conditions. The measurements, using a Princeton Applied Research (model 4500) vibrating sample magnetometer (VSM), were completed at a temperature of 20 K and in magnetic fields up to 6 kOe. The results are shown in figure 2. All the powdered samples were obtained using a hand mortar. This is not a strictly reproducible process. We did not control the grain size in the grinding process and therefore we cannot exclude that the different hysteresis loops may stem from different grain sizes.

3. Experimental results

The Mössbauer spectra of the absorbers exhibit the shape of an asymmetric doublet. The powdering of the samples resulted in powder grains with flake-like shapes that could hardly be changed. Therefore, the samples glued to a Scotch Tape exhibited inherent texture. Its value is remarkable indeed. How
much the relative ratio of the line intensities is sensitive to the sample orientation with respect to the gamma wavevector direction is demonstrated in figure 3. This offers the possibility of carrying out the data analysis similarly to how it was carried out in the case of single crystal data, and to obtain in this way additional information, unavailable for powder samples without preferred orientations. We have also performed so called ‘magic angle’ Mössbauer measurements to observe the spectrum of a texture free sample, see figure 3(c). The spectrum is a symmetric doublet and we could not detect any additional component reported in [7].

Using the transmission integral [20] in which the source width was determined in a separate calibration procedure, all the measured spectra, with different sample orientations, and with and without applied magnetic field, were fitted with a single component—the doublet. Full Hamiltonian treatment [21] was applied to the data. The quality of these fits can be seen in figure 3.

In the fitting procedure the asymmetry parameter of the electric field gradient (EFG) was set to zero because the local symmetry of the Fe atoms in the layered structure can be safely assumed to be axial. Only two parameters, namely, the main component of the EFG and the angle between the wavevector and the z-axis of the EFG were fitted. In the case of single crystal with local axial symmetry, this angle should be zero. In our case, the angle turned out to be in the range between 30° and 45°, directly related to the crystalline texture. The smaller intensity of the absorption line located at higher velocity indicates the negative sign of the EFG. The value of the nuclear quadrupole moment of the excited, \( I = 3/2 \), state of the \(^{57}\)Fe nucleus was taken from [22]. Because our data were approximated by functions related to single crystal, we performed additional measurements in an external magnetic field, see figures 3(d) and (e). Again we were able to fit the single component only. The values of magnetic induction agree within 10% with the values measured by the Hall probe, and the sign of the quadrupole splitting is negative, consistently with the results obtained in zero magnetic field.

Temperature measurements down to 13.3 K reveal neither magnetic splitting nor line broadening of the doublet. By fitting the spectra with one asymmetrical doublet it was possible to obtain the temperature dependence of the quadrupole splitting, the centre shift, the full width at half maximum of the Lorentzian lines and the ratio of areas under the lines forming the asymmetrical doublet shown in figure 4. This has been carried out for the spectra obtained in experiments performed on fresh powder and aged powder stored under Ar atmosphere as well. The data for these two experiments show small yet systematic deviations. The most important point is that the quadrupole splitting (figure 4(a)) measured in the experiment with higher statistics on the aged sample shows abnormalities and they correspond to the temperatures at which abnormalities were observed in the magnetic susceptibility measurements of the FeTe\(0.5\)Se\(0.5\) samples (figure 5), magnetite [23] and Fe\(_7\)Se\(_8\) [24]. The origin of the peak in the imaginary part of the susceptibility visible in figure 5 at 50 K is unclear. However, most likely it could be linked with the spin density anomaly. Such an anomaly was observed in transport measurements [5]. In the undoped, non-superconducting, parent Fe–Te system long-range spin density wave (SDW) order was observed near 65 K [12, 25, 26]. Short-range magnetic order in non-superconducting single crystals of Fe\(_{1+\gamma}\)Te\(_{1-\gamma}\)Se\(_x\) (\( \gamma = 0.1–0.3 \)) [27] as well as short-range magnetic order (weaker with increasing Se concentration) in superconducting single crystals with \( x = 0.25 \) and 0.3 was observed too [28]. Small systematic deviation of the centre shift of the fresh and aged samples (figure 4(b)) was observed. Data with sufficiently high statistics taken within a broad range of velocities were accumulated to observe quantitatively the amount of the impurity phases, see figure 6. An asymmetric doublet and subspectra related to Fe\(_7\)Se\(_8\), Fe\(_3\)O\(_4\) and \( \alpha \)-Fe possible phases were fitted to the spectra. Because the amount of the impurity phases is small, their hyperfine parameters were fixed. In particular, the values given in [24] and [29] were used to construct the subspectra of Fe\(_7\)Se\(_8\) and Fe\(_3\)O\(_4\), respectively. Initial fits show that the content of \( \alpha \)-Fe is below 1%. Thus in further analysis the content of \( \alpha \)-Fe was assumed to be zero; the results of the best fits are shown in figure 6 and quantitative results are collected in table 1.
Figure 4. Temperature dependence of the parameters of the main doublet. Open symbols correspond to measurements on freshly prepared powder with the planar density of the mass equal to 21(1) mg cm\(^{-2}\) while the full points show results obtained for the aged sample in Ar atmosphere (13 months) with the planar density of the mass equal to 23(1) mg cm\(^{-2}\).

Figure 5. Temperature dependence of the real part \(4\pi\chi'\)—lower panel) and imaginary part \(4\pi\chi''\)—upper panel) of the AC susceptibility for FeTe\(_{0.5}\)Se\(_{0.5}\) single crystals, measured above the superconducting transition temperature in 10 Oe of AC field with 1 and 10 kHz in warming mode.

Table 1. The relative area in the main and impurity phases determined within the transmission integral approximation. The relative area of \(\alpha\)-Fe is below 1%. The fraction of iron atoms is proportional to the ratio of the relative area and the recoil-free fraction, see text.

| Absorber               | Crystalline phase |
|------------------------|-------------------|
|                        | FeTe\(_{0.5}\)Se\(_{0.5}\) | Fe\(_2\)O\(_3\) | Fe\(_2\)Se\(_8\) |
| Fresh powder           | 80(2)             | 12(2)           | 9(2)            |
| After 19 days in air   | 85(2)             | 9(1)            | 6(1)            |
| After 4 months in air  | 83(5)             | 7(4)            | 11(4)           |
| After 6 months in air  | 84(1)             | 11(1)           | 5(1)            |
| After 16 months in air | 83.4(5)           | 10.2(2)         | 6.4(2)          |
| Stored under argon, measurement at \(T = 292\) K | 84.0(8) | 10.0(5) | 6.0(7) |
| Stored under argon, measurement at \(T = 18\) K | 83.1(7) | 8.4(5) | 8.5(5) |

argon atmosphere, the latter shows the presence of impurity phases, thus indicating that they were present also in the original bulk sample.

In order to observe the temperature dependence of the recoilless fraction, measurements in a wide velocity range were performed together with an iron foil, with both absorbers kept in the cryostat. The Fe foil of known thickness served as a precise calibration device for setting the intensity scale [30]. The ratio of the area under the doublet to the area under the Fe sextet can easily be inferred from figure 7.

4. Discussion

In the period of 16 months exposition of powdered absorber to ambient air conditions, we could not detect intuitively expected increase of the magnetite content, see figure 1 and table 1. The impurity contribution is hidden in the background for spectra measured with low statistics (figure 1(d)). It is thus clear that in order to extract the impurity phases from the main superconducting phase one has to perform the Mössbauer
Figure 6. The Mössbauer spectra of FeTe$_{0.5}$Se$_{0.5}$ samples aged in Ar, measured at (a) room temperature and (b) $T = 18$ K, fitted with four components. In (c), (d) the spectra are shown with the vertical scale enlarged and the four components are shown separately: the asymmetric doublet (most intense component), Fe$_7$Se$_8$ (moderately split component), Fe$_3$O$_4$ (mostly split component). The central data sets are difference plots between the actual spectra and fit curves.

Figure 7. The Mössbauer spectra of FeTe$_{0.5}$Se$_{0.5}$ with the planar density of the mass equal to 23(1) mg cm$^{-2}$ and iron foil, both absorbers in the cryostat, measured for determination of the recoilless fraction.

measurements with high statistics and cover a wide enough velocity range as presented in figure 6. The overlapped peaks of the impurity phases Fe$_3$O$_4$ and Fe$_7$Se$_8$ form an absorption shape similar to a flat background, see figures 6(c) and (d), which can be determined in measurements spanning a wide velocity range. On the other hand, the wide velocity range does not allow for precise determination of the doublet parameters. Thus measurements within both wide and narrow velocity ranges are required.

One could also expect, after the evidence of the easy formation of the magnetite admixture [3], that grinding at ambient conditions would cause easy oxidation of the magnetite. The magnetization loops shown in figure 2 do not support such a simple mechanism. Indeed, the grinding causes the formation of some structural defects, which apparently changes the magnetization processes seen in the case of single crystal. Surprisingly, grinding under inert gas increases the saturation magnetization whereas grinding in contact with air does not increase the value of the saturation magnetization. The results presented in table 1 show that in powder of a micrometre size, obtained from single crystal, a few per cent of the iron forms the magnetite phase and the amount of this phase remains unchanged in 16 months. Thus, one can exclude formation of magnetite as the result of chemical reaction of tetragonal FeTe$_{0.5}$Se$_{0.5}$ phase with atmospheric oxygen.

Figure 2 presents the field dependence of magnetization for FeTe$_{0.5}$Se$_{0.5}$ single crystal and powder obtained by grinding under argon and ambient conditions recorded at 20 K in a magnetic field of up to 6 kOe. The value of the saturation magnetization, $M_s$, for the studied monocrystal is about 1 emu g$^{-1}$. The saturation magnetization of Fe$_7$Se$_8$, determined by Kamimura [31] at 80 K is about 85 emu cm$^{-3}$, which corresponds to about 14 emu g$^{-1}$. Taking into account that the difference between the saturation magnetization at 80 and at 20 K is insignificant, we can estimate that the maximum volume fraction of the Fe$_7$Se$_8$ phase in the studied sample does not exceed 7%. Its correlates well with the 5.35(40)% estimation of the volume fraction for the impurity hexagonal Fe$_7$Se$_8$ phase (space group $P6_3/mmc$) in FeTe$_{0.5}$Se$_{0.5}$ obtained from neutron powder diffraction measurements performed on similar crystal [32]. The saturation magnetization of Fe$_3$O$_4$ nanoparticles depends on their size and decreases with decreasing nanoparticle size. For the smallest nanoparticles with the size of about 5 nm, the magnetization at 20 K in a magnetic field of 6 kOe is about 40 emu g$^{-1}$ [33]. This means that the volume fraction of the impurity Fe$_3$O$_4$ phase in the studied sample cannot be higher than 2.5%. The powder x-ray data for the studied samples do not show peaks either for Fe$_7$Se$_8$ or for Fe$_3$O$_4$, which gives an upper estimation of their volume fraction to be 5%.

Mechanically formed absorbers from the powder of FeTe$_{0.5}$Se$_{0.5}$ show remarkable crystalline texture, similar in all the absorbers prepared in this project, see the examples in figure 4(d). This is observed in our powder x-ray measurements as enhanced intensities of the (00l) Bragg peaks, reported earlier by Bendele et al [32] in a neutron powder diffraction experiment.
Fe$_3$O$_4$ and Fe$_7$Se$_8$ phases were detected in the investigated samples. The relative amounts of these compounds were determined by fitting a function which is the sum of the subspectra with shapes as given in the publications [24, 29]. The area under the Fe$_7$Se$_8$ subspectrum strongly increases with decreasing temperature. This is an indication that Fe$_7$Se$_8$ forms small superparamagnetic particles. Indeed, at low temperature all the Fe$_7$Se$_8$ particles show magnetic splitting seen as the subspectrum in figure 6(d). At room temperature a fraction of the Fe$_7$Se$_8$ particles is thermally activated and does not show the magnetic splitting present in bulk Fe$_7$Se$_8$ sites. The thermally activated fraction contributes to the main doublet in the Mössbauer spectrum. Because the isomer shift and the quadrupole splitting of Fe$_7$Se$_8$ sites are different from the those of FeTe$_{0.5}$Se$_{0.5}$, the shape of the main doublet is thus slightly distorted. Our results are also in agreement with neutron measurements performed on single crystal of FeTe$_{0.5}$Se$_{0.5}$, where Fe$_7$Se$_8$ was detected [32], as well as with the Mössbauer and x-ray measurements performed on a polycrystalline sample of FeTe$_{0.5}$Se$_{0.5}$, where Fe$_7$Se$_8$ was detected too [7].

The shape of the main FeTe$_{0.5}$Se$_{0.5}$ component agrees with the one reported for FeSe [3, 34, 35]. We do not observe magnetic order at Fe sites. Small abnormalities are observed at various temperatures. They are observed for the quadrupole splitting at temperatures of about 70 and 100 K (figure 4(a)), in a jump of the full width at half maximum at temperatures of about 50 K (figure 4(c)), and a maximum in asymmetry of the main doublet at temperatures of about 130 K (figure 4(d)). These abnormalities were not detected in the first experiments performed with lower statistics (open points in figure 4). There are two possible explanations of these observations. The first one is the possibility of the tetragonal to orthorhombic structural phase transition reported in [36] for FeSe at $T$ of about 70 K or at $T$ of about 100 K [37], and for Fe$_{1+y}$Te$_{0.5}$Se$_{0.5}$ at $T$ of about 40 K [38]. Orthorhombic distortion can naturally lead to a change in the electric field gradient acting on the $^{57}$Fe nucleus, resulting in changes of the quadrupole splitting. However, because the observed changes are small, one cannot exclude another possibility that the detected unambiguous impurity phases of Fe$_3$O$_4$ and Fe$_7$Se$_8$ are responsible for the observed non-monotonic variation of the hyperfine parameters. Fe$_3$O$_4$ exhibits the Verwey transition at about $T = 120$ K while Fe$_7$Se$_8$ undergoes spin reorientation at $T = 125$ K. At the phase transition points a change of the shape of the absorption spectrum occurs, influencing slightly the shape of the asymmetric doublet fitted to the spectra. Also, as already explained, the presence of a fraction of superparamagnetic particles changes the shape of the main doublet.

A temperature change of the isomer shift at $T = 105$ K in superconducting FeSe was reported in [35]. Within the experimental precision we could not detect any peculiarities at this temperature in measurements on fresh powders or in measurements performed with higher statistics on aged samples (figure 4(b)). Instead, a systematic difference is observed between the isomer shifts of fresh and aged in argon samples, and its origin remains unclear.

The sign of the EFG is found to be negative in agreement with [35]. Fitting the $(1-aT^{3/2})$ dependence to the quadrupole splitting shown in figure 4(a) one arrives at $a = 3.3 \times 10^{-7}$ K$^{-3/2}$ falling in the typical range predicted by molecular dynamics calculations [39].

The Lamb–Mössbauer fraction does not show any peculiarities within the experimental accuracy. However, neither Debye nor Einstein model predictions [40] fit the data shown in figure 8. This type of behaviour is observed in some systems and can be parameterized by temperature dependence of the Debye temperature [41, 42]. Our results correspond to recently reported anomalies observed in FeTe$_{0.5}$Se$_{0.5}$, where the Debye temperature determined from the temperature dependence of the Lamb–Mössbauer factor was lower by about 200 K than those determined from the second order Doppler shift [7]. We also note that clearly nonharmonic behaviour of the Fe dynamics was shown in layered LiFeAs superconductor [17].

The absolute values of the recoilless fraction allow a quantitative estimation of the magnetite impurity phase. At room temperature 12(2)% of the area corresponds to magnetite while 80(2)% to the tetragonal FeTe$_{0.5}$Se$_{0.5}$ phase (first row data, table 1). The relative area is proportional to the concentration of $^{57}$Fe per unit area and to the recoilless fraction. Taking the recoilless fractions of magnetite $f_m = 0.89(4)$ [43], and of the tetragonal phase $f_{tet}$ from figure 8 ($f$ at $T = 295$ K), the ratio of the amount of iron atoms in magnetite to the amount of iron atoms in the tetragonal phase is $(f_{tet}/f_m)(12(2)%)/(80(2)% = 0.035(6)$.

Another estimation, in which the previously estimated recoilless fraction is not explicitly used, comes from figure 1. A magnetite sample with known thickness was used in this measurement. Analysis of the spectra in figure 1(f) results in an area of magnetite equal to 52% whereas 42% of the total area is due to the tetragonal phase. These values correspond to the amount of tetragonal phase 21(1) mg cm$^{-2}$ and extra magnetite 3.6 mg cm$^{-2}$ (the small amount of magnetite present in the original sample is neglected). The ratio of masses is proportional to the ratio of areas, 3.6/21(1) = $x$52/42, where $x$ is some constant. In figure 1(a) the area of magnetite is equal to 12(2)% and the area of the tetragonal phase is 80(2)%. Similarly, one can write another proportionality: $s/21(1) =$...
12(2)/80(2)x with s being the planar density of mass of the magnetite in the sample corresponding to figure 1(a). One thus gets $s = (3.6 \text{ mg cm}^{-2}(12(2)/80(2)) \cdot (42/52) = 0.44 \text{ mg cm}^{-2}$. Thus, for 0.44 mg cm$^{-2}$ of FeO$_4$ and 21(1) mg cm$^{-2}$ of FeTe$_{0.5}$Se$_{0.5}$, one finds the ratio of Fe atoms in these two phases to be equal to 0.043(7). The two estimations are consistent within the experimental uncertainty and show also that the low value of the recoilless fraction presented in figure 8 enhances the relative area of the magnetite in the Mössbauer spectra. The Mössbauer estimations of the magnetite content are also consistent with results obtained from magnetization and diffraction measurements.

5. Conclusions

Experiments performed on powdered single crystals of FeTe$_{0.5}$Se$_{0.5}$ within a broad velocity range revealed the presence of minor content of two impurity phases: FeO$_4$ and Fe$_3$Se$_8$. We have shown that the quantitative estimation of the magnetite impurity phase is consistent with the anomalously small value of the recoilless fraction of tetragonal FeTe$_{0.5}$Se$_{0.5}$. The content of the Fe$_2$Se$_5$ phase obtained from fits with hyperfine parameters related to bulk crystals depends strongly on temperature, indicating its superparamagnetic behaviour. An increase of the magnetite content is not observed within a period of 16 months exposition of the sample to air conditions. Mechanical grinding apparently influences the shape of the magnetization loops. Grinding under ambient air does not increase the saturation magnetization in contrast to grinding under inert gas. The asymmetry of the absorption lines in the Mössbauer spectra depends on the sample orientation with respect to the wavevector of the radiation, indicating strong crystalline texture induced easily during absorber preparation. The samples stored in Ar atmosphere show a small increase of the isomer shift of the doublet. The small peculiarities observed for the temperature dependence of the hyperfine parameters can be explained as due to either possible orthorhombic distortion similar to that observed in FeSe [36] or the temperature behaviour of the impurity phases FeO$_4$ and Fe$_3$Se$_8$.

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