Growth conditions, structure and superconductivity of pure and metal-doped FeTe$_{1-x}$Se$_x$ single crystals

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Abstract

Superconducting single crystals of pure FeTe$_{1-x}$Se$_x$ and FeTe$_{0.65}$Se$_{0.35}$ doped with Co, Ni, Cu, Mn, Zn, Mo, Cd, In, Pb, Hg, V, Ga, Mg, Al, Ti, Cr, Sr or Nd into Fe ion sites have been grown applying Bridgman’s method. It has been found that the sharpness of the transition to the superconducting state in FeTe$_{1-x}$Se$_x$ is evidently inversely correlated with the crystallographic quality of the crystals. Among all of the studied dopants only Co, Ni and Cu substitute Fe ions in FeTe$_{0.65}$Se$_{0.35}$ crystals. The remaining ions examined do not incorporate into the crystal structure. Nevertheless, they form inclusions together with selenium, tellurium and/or iron, which change the chemical composition of the host matrix and therefore influence the $T_c$ value. The small disorder introduced into the magnetic sublattice, by partial replacement of Fe ions by a slight amount of nonmagnetic ions of Cu ($\sim 1.5$ at.%$)$ or by magnetic ions of Ni ($\sim 2$ at.%$)$ and Co ($\sim 5$ at.%$)$ with spin values different than that of the Fe ion, completely suppresses superconductivity in the FeTe$_{1-x}$Se$_x$ system. This indicates that, even if superconductivity is observed in the system containing magnetic ions, it cannot survive when the disorder in the magnetic ion sublattice is introduced, most likely because of magnetic scattering of Cooper pairs.

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

1. Introduction

The simple chemical formula and simple crystallographic structure are the reasons to consider the non-stoichiometric iron selenide FeSe$_{1-\delta}$ as a model system for the investigations of the mechanism of superconductivity in iron-based superconductors. Under high pressure, the critical temperature ($T_c$) for this compound increases from $\sim 8.5$ up to $\sim 37$ K [1–4]. Quite likely, a similar effect may be achieved by appropriate isovalent substitution since chemical pressure, caused by tellurium substitution into selenium sites, raises the critical temperature in FeTe$_{0.35}$Se$_{0.65}$ up to $\sim 15$ K [5, 6]. Unfortunately, FeTe$_{0.35}$Se$_{0.65}$ exhibits the coexistence of two tetragonal phases [7–9]. However, the materials with lower selenium content and with slightly lower transition temperature than that of FeTe$_{0.35}$Se$_{0.65}$ may be grown as a single-phase crystal. A lot of chemical substitutions into FeTe$_{1-x}$Se$_x$ were already reported. Most of the work was done on polycrystalline samples and it was assumed quite often that the analysed final chemical composition is identical to that of the mixture of starting chemicals. Therefore, in order to re-examine critically the very wide spectrum of possible metal substitutions, we have decided to grow single crystals of FeTe$_{1-x}$Se$_x$ substituted with various metals into the Fe position.

The recent report by Wu et al [10] described the effect of various metals’ ion substitution, such as Al, Ti, V, Cr, Mn, Co, Ni, Cu, Ga, In, Na, Ba and Sm into superconducting FeSe$_{1-\delta}$, obtained by a solid state reaction. The authors claimed that
indium does not substitute properly for Fe and an additional InSe phase was observed. The 10 at.% of Ba substituted into the FeSe$_{1-x}$ sample destroys crystallinity. Substitution over 25 at.% of Ga or Sm causes phase separation. The tetragonal structure was retained with substitution of 10 at.% of Ga and Sm, as well as with 25 at.% of Al. Impurities, found by x-ray analysis, were described as an additional hexagonal phase or as binary metal selenides. All of the examined transition metals (Ti, V, Cr, Mn, Co, Ni and Cu) were found to be incorporated into the FeSe structure as long as their content does not exceed 10 at.%. In previous studies, substitution of Co, Ni, Cu and Mn ions into the Fe–Se system was reported as well [11–14]. It was found that Fe ions were successfully substituted by Co up to 50 at.% [14] while the limit of solubility of Cu in FeSe$_{1-x}$ reached the range 20–30 at.% [15]. On top of that, successful intercalation with 10 at.% of sodium was reported too [16].

On the other hand, it was found that FeSe$_{1-x}$ with Fe substituted by 10 at.% of Ti, V, and Cr is no longer superconducting [10]. Only the Fe$_{1-x}$Cu$_x$Se$_{1-x}$ samples with $x$ up to 0.02 exhibit superconductivity, shown in transport measurements, while those with $x$ over 0.03 show semiconducting behaviour [10, 11]. The above results agree with those published by Williams et al [15]. However, it was found that DC magnetic susceptibility shows no evidence of bulk superconductivity even for Fe$_{0.995}$Cu$_{0.005}$Se, i.e. for the sample with Cu content as low as 1.5 at.%. Similar behaviour was observed for the Fe$_{1-x}$Ni$_x$Se$_{1-x}$ system with 0.01 < $y$ < 0.1 [12, 13]. According to Mizuguchi et al [13], the onset of critical temperature measured by resistivity ($T_{\text{res.onset}}$) was estimated to be 10 K for the sample with $y = 0.05$. Zhang et al [12] reported the offset of critical temperature ($T_{\text{res.offset}}$) below 2 K for the sample with $y = 0.01$ and no superconducting transition above 2 K for the sample with $y = 0.04$. For Fe$_{1-x}$Co$_x$Se$_{1-x}$, $T_{\text{res.onset}}$ was estimated to be equal to 10 and to 5 K for the samples with $z$ equal to 0.05 and 0.1, respectively [13]. For the sample with $z = 0.025$, $T_{\text{res.onset}}$ was observed at around 2 K. It was reported that the FeSe$_{1-x}$ samples substituted with Co concentrations higher than 2.5 at.% are no longer superconducting [14]. These results contrast with those of Liu et al [16], where Fe$_{0.95}$Co$_{0.05}$Se$_{1-x}$ was reported to be superconducting with $T_c$ being even higher than that of FeSe$_{1-x}$.

Generally, the superconducting transition temperature for FeSe$_{1-x}$ substituted with isovalent Co, Ni and Cu ions was found to be strongly suppressed, whereas, surprisingly, substitution with Mn with concentrations up to 30 at.% changed the $T_c$ value only slightly. However, nonisovalent dopants like Al, Ga and Sm influence $T_c$ differently. A drop in $T_{\text{res.onset}}$ at about 8.5 K and at about 6.8 K was observed for FeSe$_{1-x}$ doped with 10 at.% of Al and with 20 at.% of Ga, respectively. In contrast, substitution of 10 at.% of Sm raised $T_{\text{res.onset}}$ slightly to about 10.6 K, but then at the substitution of 20 at.% $T_{\text{res.onset}}$ dropped to 9.2 K. Interestingly, a similar drop in $T_{\text{res.onset}}$ to the value of 10.6 K was observed in FeSe$_{1-x}$ doped with 10 at.% of Ba [10, 11].

Recently, Kotegawa et al [17] reported that $^{77}$Se-NMR measurements performed on FeSe substituted with Co indicate the electron doping to the system. Since strong spin fluctuations disappear in (Fe$_{0.9}$Co$_{0.1}$)Se, the electron doping was considered to modify the Fermi surface, resulting in the collapse of the nesting in FeSe.

Polycrystalline FeTe$_{0.5}$Se$_{0.5}$ samples doped with 5 at.% of Mn, Co, Ni, Cu and Zn were explored by Zhang et al [18]. It was found that among the studied substitutions only Zn ions do not incorporate into the host lattice and most likely ZnSe formation takes place. Despite that, both the pure and the samples doped with Zn exhibited similar transition temperature to the superconducting state both in magnetic and transport measurements. Pure tetragonal phases of FeTe$_{0.5}$Se$_{0.5}$ substituted with Cu, Ni, Co and Mn into the Fe site were obtained according to powder x-ray diffraction results. It was claimed that superconducting properties are extremely sensitive to a kind of substituted metal. Superconductivity is destroyed completely in the samples with Ni and Cu substitution, in contrast to those substituted with Mn and Co, where according to the transport and magnetic measurements the $T_c$ value is altered only slightly. Shishra et al [19] reported successful iron substitution in FeTe$_{0.5}$Se$_{0.5}$ by Ni and Co up to 10 at.%. They found that for both Co- and Ni-substituted systems strong suppression of superconducting transition temperature takes place. Successful intercalation with up to 100 at.% of lithium by the electrochemical technique was reported too [20].

All of the samples with various elements substituting Fe in both systems of FeSe and FeTe$_{1-x}$Se$_x$ described so far were prepared by conventional solid state reaction. Only in the work of Williams et al [15] were polycrystalline samples with partial substitution of Fe by Cu in the Fe–Se system studied, prepared by the liquid phase reaction.

According to the phase diagram of the Fe–Se system [21], it is difficult to obtain large single crystals of the superconducting FeSe$_{1-x}$ phase using one of the techniques of growth from the melt. The isostructural, pseudobinary Fe–Te–Se system relatively easily crystallizing from the melt is much more promising for the successful growth of substituted single crystals. So far, growth of superconducting FeTe$_{1-x}$Se$_x$ single crystals using Bridgman’s method was reported by different groups [7–9, 22–32] but there is a lack of data concerning any substitution into the Fe site.

In this paper, the growth of FeTe$_{1-x}$Se$_x$ single crystals doped with various metals is reported. Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) have allowed us to determine unequivocally which of the dopants are incorporated into the host lattice. The influence of chemical doping at the Fe site, by various elements, on the superconducting transition temperature has been determined.

2. Experimental procedure

Superconducting single crystals of FeTe$_{1-x}$Se$_x$ ($x = 0.3–0.55$) and FeTe$_{0.65}$Se$_{0.35}$ doped with Co, Ni, Cu, Mn, Zn, Mo, Cd, In, Pb, Hg, V, Ga, Mg, Al, Ti, Cr, Sr and Nd have been grown using Bridgman’s method. All FeTe$_{1-x}$Se$_x$ samples were prepared from stoichiometric quantities of iron chips
(3N5), tellurium powder (4N) and selenium powder (pure). Double-walled evacuated sealed quartz ampoules containing the starting materials were placed in a furnace with a vertical gradient of temperature equal to 1.2–2 °C mm⁻¹. 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 with steps of 1–2 °C h⁻¹ and next to 200 °C at the rate of 60 °C h⁻¹, and finally cooled down to room temperature with the furnace. Proper adjustment of cooling velocity and/or vertical gradient of temperature in the furnace allowed us to tune the growth velocity in the range from 0.5 to 8 mm h⁻¹, permitting the growth of single crystals of various crystallographic qualities. The obtained crystals exhibited a cleavage plane (001) with random orientation with respect to the growth direction. The single crystals of the highest crystallographic quality exhibited well-developed (100) and (101) natural planes.

In order to obtain FeTe₀.₆₅Se₀.₃₅ single crystals substituted with various metals, the following chemicals were added: 0.5–20 at.% of Co (metallic), NiSe (pure) and CuSe (4N), 2.5–20 at.% of Mn pieces (5N), 1 at.% of Al, Ga, In, Nd (5N), HgSe powder (5N) and 5 at.% of Mg pieces (5N), Ti, V, Cr, Mo pieces (5N), Sr pieces (2N), ZnSe, CdSe powder (5N), and PbTe powder (pure).

The chemical composition of the matrix and inclusions in pure and doped single crystals was checked on the cleavage plane of the crystals by field emission scanning electron microscopy (FESEM, JEOL JSM-7600F operating at 20 kV). The quantitative point analysis was performed by Oxford INCA energy dispersive x-ray spectroscopy (EDX) coupled with the SEM. Phase analysis and structural refinement of the crystals were performed at room temperature by x-ray powder diffraction (XRPD) using Ni-filtered Cu Kα radiation with a Siemens D5000 diffractometer. The precision value of the c lattice constant and the Δω value of the ω scan on the 004 diffraction line were obtained in single-crystal measurements on the well-defined, natural cleavage (001) plane. The diffraction patterns were analysed by the Rietveld refinement method using the DBWS-9807 program [33]. The c lattice constant obtained in single-crystal measurements was used as a fixed value in powder Rietveld analysis for the determination of other structural parameters, i.e. a, V and occupation number. Data on powdered single crystals were collected in the angular range 2θ < 2θ < 100° with steps of 0.02° and averaging time of 10 s/step. All the reflections were indexed to a tetragonal cell in the space group P4/mnm (no. 129) of the PbO structural type with occupation Wyckoff’s 2a site by Fe and 2c site by Se/Te. It was assumed additionally that an excess of Fe ions occupies 2c sites of the structural vacancy in the Se/Te plane. The measurements of AC magnetic susceptibility (field amplitude 1 and 10 Oe, frequencies 1 and 10 kHz) for all of the samples were performed with a physical property measurement system (PPMS) from Quantum Design.

3. Results and discussion

3.1. Structural analysis and superconducting transition temperature for FeTe₁₋ₓSeₓ (0.3 < x < 0.55) single crystals

Lattice parameters and unit cell volume for the crystals of FeTe₁₋ₓSeₓ prepared under different conditions are limited to a narrow range. No impurity phase was observed for all of the obtained crystals. For the crystals with x = 0.35, the average lattice constant values are equal to a = 3.8014 Å, c = 6.0913 Å and V = 88.021 Å³, and the c/a ratio is close to 1.6024. Since the c lattice constant strongly depends on the selenium concentration [1, 7, 10, 12, 23–31, 33–45], as one can see in figure 1, it is easy to check if segregation of Se/Te occurs during the crystallization process. We determined the value of the c lattice constant at the beginning and at the end of the selected single crystals. Our results have confirmed that changes of the c lattice constant along the crystal growth direction are negligible. Small inclusions of iron oxides were observed on natural cleavage planes. Initial chemical compositions in the crystallization process compared with chemical compositions, estimated by EDX analysis, and crystallographic data for the grown FeTe₁₋ₓSeₓ single crystals are collected in table 1. For FeTe₀.₅Se₀.₅, a noticeable difference between initial and estimated by EDX chemical composition as well as broadening of the 004 diffraction peak (∆ω), are probably connected with separation of phases with different Se/Te ratios, as observed in [7–9]. It should be noted that only small fluctuations of the Se/Te ratio were observed for the samples with x = 0.35.

The critical temperature Tc^{ost} of superconducting FeTe₁₋ₓSeₓ single crystals changes from ~12 K for x ~ 0.3 to ~14.7 K for x ~ 0.5, in agreement with the results of

Table 1. Summary of the chemical composition and structural parameters for selected single crystals of FeTe₁₋ₓSeₓ.

| Starting composition | Composition by EDX (±0.02) | a (Å) | c (Å) | V (Å³) | Δω (min) |
|----------------------|----------------------------|-------|-------|--------|---------|
| FeTe₀.₅Se₀.₅          | Fe₀.₉₈Te₀.₅₁Se₀.₄₁          | 3.7992| 6.0560| 87.412 | 16.65   |
| FeTe₀.₆₅Se₀.₃₅        | Fe₀.₉₉Te₀.₅₅Se₀.₄₁          | 3.8036| 6.0921| 88.137 | 6.00    |
| FeTe₀.₇₅Se₀.₂₅        | Fe₀.₉₇Te₀.₅₃Se₀.₄₁          | 3.7985| 6.0918| 87.896 | 3.28    |
| FeTe₀.₈₅Se₀.₁₅        | Fe₀.₉₆Te₀.₅₁Se₀.₃₅          | 3.8012| 6.0874| 87.958 | 2.52    |
| FeTe₀.₉₅Se₀.₀₅        | Fe₀.₉₅Se₀.₂₃               | 3.8020| 6.0937| 88.086 | 1.67    |
| FeTe₁₆Se₀₃            | Fe₀.₉₆Te₀.₇₅Se₀.₃₃          | 3.7995| 6.1265| 88.443 | 2.7     |
analysis of the data presented in the plot. Demagnetizing field correction was not taken into account in the
and 0.5), measured in 10 Oe AC field with 1 kHz in warming mode. The correction for a

demagnetizing field was not taken into account in the analysis of the data presented in the plot.

the previous report [34] (see figure 2). The correction for a
demagnetizing field was not taken into account in the analysis of the data for temperature dependence of the AC susceptibility and therefore the absolute value of the presented real part of AC susceptibility is higher than one.

For the selenium concentration \( x = 0.35 \), we obtained high quality single-phase crystals with a critical temperature \( T_{c\text{onset}} \) of about 12.5 K. Full width at half-maximum (FWHM) of the 004 diffraction peak for the highest crystallographic quality single crystals of FeTe\(_{0.65}\)Se\(_{0.35}\) has been found to be as small as \( \Delta\omega \approx 1.35 \) arc min. It is found that the sharpness of the transition to the superconducting state is strongly correlated with the crystallographic quality as is shown in figure 3. The crystals characterized with \( \Delta\omega \) values equal to 1.67, 2.52, 3.28 and 6.00 arc min have been grown at the velocities of \( \sim 1.2, \sim 1.8, \sim 5 \) and \( \sim 8 \) mm h\(^{-1}\), respectively. Since the investigated samples were different in shape the impact of the demagnetizing field on AC susceptibility varied among them, as one can see in figure 2. Therefore, for comparison of the sharpness of the superconducting state transition, the data of 4\(\pi\chi'\) presented in figure 3 were normalized to the value of \(-1\) for the real part of AC susceptibility at low temperatures.

It was found that the narrowest transition to the superconducting state (width \( \sim 0.6 \) K) exhibits single crystals with relatively large values of \( \Delta\omega \) equal to 6 arc min. Furthermore, the decrease in the \( \Delta\omega \) value is correlated with the increase of the width of the transition (90%–10% criterion). This correlation found for almost all of the single crystals studied is not fully understood at present. It suggests that disorder is a necessary ingredient of the superconducting state in the FeTe\(_{1-\delta}\)Se\(_x\) system and in any case it indicates at least that properties of FeTe\(_{1-\delta}\)Se\(_x\) are very sensitive to the defects present in the sample [35, 46, 47]. It means that the existence of defects in single crystals may support superconductivity.

3.2. Chemical substitution at Fe site by Co, Ni, Cu, Mn, Zn, In, Pb, Hg, Cd, M, Mg, V, Ga, Al, Ti, Cr, Sr and Nd in FeTe\(_{0.65}\)Se\(_{0.35}\) single crystals

The composition FeTe\(_{0.65}\)Se\(_{0.35}\) was chosen to study the effect of chemical substitution into Fe site in the FeTe\(_{1-\delta}\)Se\(_x\) system and single crystals with Co, Ni, Cu, Mn, Zn, Cd, In, Pb, Hg, V, Ga, Mg, Al, Ti, Cr, Sr or Nd dopants were grown using Bridgman’s method. We have found that only the Co, Ni and Cu ions are properly incorporated into the host matrix. Substitution of Ni and Cu up to 20 at.% does not lead to the appearance of any visible indication of phase separation and does not damage crystallinity. However, cobalt–iron–telluride inclusions are found in crystals with higher Co concentrations. The analysis of the chemical composition of the matrix allowed us to conclude that above 10 at.% of Co competitive reaction of Co–Te takes place and the limit of solubility of Co ions in the FeTe\(_{0.65}\)Se\(_{0.35}\) crystals is equal to about 15 at.%. The SEM image of the cleavage plane of the matrix of Fe–TM–Te–Se, where TM is a transition metal, indicates the appearance of small iron oxide inclusions, as is presented in figure 4.

The tetragonal structure of the single crystals obtained substituted with Co, Ni and Cu was confirmed by room-temperature x-ray data analysis. Full width at half-maximum (FWHM) of the \( \omega \) scan on the 004 peak for the highest crystallographic quality single crystals substituted with Ni is found to be \( \Delta\omega = 1.25 \) arc min (figure 5). The data presented

![Figure 2](image1.png)

**Figure 2.** Real part (4\(\pi\chi'\)—lower panel) and imaginary part (4\(\pi\chi''\)—upper panel) of AC magnetic susceptibility as a function of temperature for selected single crystals of FeTe\(_{1-\delta}\)Se\(_x\) \((x = 0.3, 0.35\) and 0.5\), measured in 10 Oe AC field with 1 kHz in warming mode. The composition FeTe\(_{0.65}\)Se\(_{0.35}\) was chosen to study the effect of chemical substitution into Fe site in the FeTe\(_{1-\delta}\)Se\(_x\) system and single crystals with Co, Ni, Cu, Mn, Zn, Cd, In, Pb, Hg, V, Ga, Mg, Al, Ti, Cr, Sr or Nd dopants were grown using Bridgman’s method. We have found that only the Co, Ni and Cu ions are properly incorporated into the host matrix. Substitution of Ni and Cu up to 20 at.% does not lead to the appearance of any visible indication of phase separation and does not damage crystallinity. However, cobalt–iron–telluride inclusions are found in crystals with higher Co concentrations. The analysis of the chemical composition of the matrix allowed us to conclude that above 10 at.% of Co competitive reaction of Co–Te takes place and the limit of solubility of Co ions in the FeTe\(_{0.65}\)Se\(_{0.35}\) crystals is equal to about 15 at.%. The SEM image of the cleavage plane of the matrix of Fe–TM–Te–Se, where TM is a transition metal, indicates the appearance of small iron oxide inclusions, as is presented in figure 4.

![Figure 3](image2.png)

**Figure 3.** Temperature dependence of real part (lower panel) and imaginary part (upper panel) of AC magnetic susceptibility, normalized to the ideal value of \(-1\) for the real part of AC susceptibility, measured in 1 Oe AC field with 10 kHz in warming mode for selected FeTe\(_{0.65}\)Se\(_{0.35}\) single crystals with various values of \( \Delta\omega \) (listed in table 1).
Figure 4. Photograph of Fe$_{0.995}$Co$_{0.005}$Te$_{0.65}$Se$_{0.35}$ ($\Delta\omega = 1.92$ arc min) single crystal with visible natural (100) and (001) planes marked by arrows (a) and SEM images of the (100) crystal plane (b) compared with SEM images of the natural cleavage (001) plane for the crystals with different substituent metal ion concentrations and with different Te/Se ratios: Fe$_{0.995}$Ni$_{0.005}$Te$_{0.65}$Se$_{0.35}$ ($\Delta\omega = 2.45$ arc min) (c) and Fe$_{0.95}$Cu$_{0.1}$Te$_{0.75}$Se$_{0.25}$ ($\Delta\omega = 2.93$ arc min) (d). Arrows in the SEM images mark iron oxide inclusions. White spacers below images indicate a distance of 10 $\mu$m ((b), (d)) and 100 $\mu$m (c).

Figure 5. Room-temperature x-ray spectra from single-crystal measurements on natural cleavage (001) plane of Fe$_{0.95}$Ni$_{0.05}$Te$_{0.65}$Se$_{0.35}$: doublet (K$\alpha_1$–K$\alpha_2$) of 004 Bragg peak obtained in $\omega/2\theta$ scan (left panel) and rocking curve in $\omega$ scan measurements of 004 peak, with refined value of the full width at half-maximum (FWHM $\equiv \Delta\omega$) equal to 1.25 arc min (right panel), in panel (a) were obtained with both K$\alpha_1$ and K$\alpha_2$ irradiation and therefore two maxima are visible.

It was found that the value of the $c$ lattice constant decreases linearly with increasing Co, Ni and Cu ion concentration, as is shown in figure 6. The most significant changes in the $c$ value are due to copper ion substitution into the Fe site while the impact of cobalt substitution is the smallest.

Negligible segregation of Se/Te in the Fe–Te–Se system allowed us to check if the segregation between Fe and Ni or Cu takes place. We have compared the value of the $c$ lattice constant at the beginning and at the end of the grown single crystals substituted with 20 at.% of Ni and Cu. The obtained results confirm (see table 2) that the changes of the $c$ lattice

Figure 6. The $c$ lattice constants of Fe$_{1-y}$TM$_y$Te$_{0.65}$Se$_{0.35}$ (TM = Co, Ni and Cu) as a function of dopant content $y$. The $y$ value is equal to the initial dopant concentration.
constant along the crystal growth direction are negligible, which means that the segregation is negligible. There is a difference between the values of the lattice constant at the beginning and at the end of the crystal substituted with 20 at.% of Co since 20 at.% of Co is above the limit of Co solubility in the Fe–Te–Se system.

Substitution of manganese and zinc leads to the creation of inclusions of metal selenides and to a change of Se/Te ratio in the host lattice, as found by SEM/EDX. Substitution of manganese leads to the formation of an additional compound of (MnFe)₂O₃ type, as identified by SEM/EDX analysis. X-ray analysis indicates the presence of a cubic MnSe phase (space group Fm3m) with average lattice constant of 5.470 Å despite MnSe inclusions not being detected with SEM. The appearance of the MnSe phase in single crystals is in agreement with the changes of matrix composition determined from SEM/EDX analysis. Substitution of cadmium and indium leads to the creation of inclusions of CdTe or InTe type, whereas substitution of molybdenum leads to the creation of MoTe₈₋ₓSeₓ compounds. Substitution of lead and mercury leads to the formation of metal-iron-telluride alloys. Substitution of vanadium and gallium leads to the formation of alloys with iron. As a result of the appearance of such iron-rich alloys, the concentration of iron in the matrix is decreased. Magnesium reacts with quartz in the ampoule wall and magnesium silicate compounds appear. Typical SEM images of FeTe₀.₆₅Se₀.₃₅ matrix and inclusions of ZnSe, Mo(Se₃Te₅)₂, V₀.₆₃Fe₀.₃₅ and Ga₀.₆Fe₀.₄ are shown in figure 7.

It was found that the remaining added elements, i.e. Al, Ti, Cr, Sr and Nd, do not incorporate into the host lattice of FeTe₀.₆₅Se₀.₃₅ single crystals. Non-reacted inclusions with Al, Ti, Cr, Sr and Nd were found only at the end of the ingots. It means that composition of the matrix is not changed significantly during crystallization. A summary of chemical compositions of the matrix and inclusions in FeTe₀.₆₅Se₀.₃₅ single crystals doped with the elements that do not incorporate into the host lattice is shown in table 3.

### Table 2

Summary of the chemical composition, structural parameters and critical temperature for selected single crystals of Fe₁₋ₓTMₓTe₀.₆₅Se₀.₃₅ (TM = Co, Ni and Cu, 0.005 < y < 0.2). The critical temperature T° onset (10% criterion) was determined from the measurements of AC magnetic susceptibility (field amplitude 1 Oe, frequency 10 kHz) performed with a physical property measurement system (PPMS). Symbol <? in the column with T° onset means that no trace of superconductivity was detected in the measurements for T° > 2 K.

| At.% of dopant | Composition by EDX (±0.02) | a (Å)  | c (Å)  | Δα (min) | T° onset (K) |
|---------------|-----------------------------|--------|--------|----------|--------------|
| 0.5 at.% of Co | Fe₀.₉₅Co₀.₀₅Te₀.₆₅Se₀.₃₄   | 3.7992 | 6.0902 | 1.92     | 11.9         |
| 1 at.% of Co  | Fe₁₀Co₀Te₀.₆₅Se₀.₃₄         | 3.8034 | 6.0868 | 1.25     | 11.4         |
| 1.5 at.% of Co| Fe₁₀Co₀.₅Te₀.₆₅Se₀.₃₄       | 3.8027 | 6.0864 | 1.85     | 10.9         |
| 2 at.% of Co  | Fe₀.₉₈Co₀.₀₂Te₀.₆₄Se₀.₃₆     | 3.8021 | 6.0810 | 2.75     | 10.2         |
| 2.5 at.% of Co| Fe₀.₉₆Co₀.₀₅Te₀.₆₃Se₀.₃₅     | 3.8007 | 6.0834 | 1.82     | 9.5          |
| 3 at.% of Co  | Fe₀.₉₄Co₀.₀₇Te₀.₆₂Se₀.₃₅     | 3.8044 | 6.0828 | 2.15     | 8.7          |
| 3.5 at.% of Co| Fe₀.₉₂Co₀.₀₉Te₀.₆₁Se₀.₃₅     | 3.8005 | 6.0817 | 2.03     | 8.2          |
| 4 at.% of Co  | Fe₀.₉₅Co₀.₁₁Te₀.₆₃Se₀.₃₅     | 3.7994 | 6.0794 | 1.82     | 7.2          |
| 4.5 at.% of Co| Fe₀.₉₀Co₀.₁₂Te₀.₆₄Se₀.₃₄     | 3.8017 | 6.0846 | 1.85     | <?           |
| 5 at.% of Co  | Fe₀.₈₅Co₀.₁₅Te₀.₆₆Se₀.₃₃     | 3.8025 | 6.0792 | 1.82     | <?           |
| 10 at.% of Co | Fe₀.₇₅Co₀.₂₅Te₀.₆₅Se₀.₃₄     | 3.7996 | 6.0662 | 2.85     | <?           |
| 15 at.% of Co | Fe₀.₇₅Co₀.₃₅Te₀.₆₄Se₀.₃₄     | 3.7986 | 6.0545 | 2.03     | <?           |
| 20 at.% of Co | Fe₀.₇₅Co₀.₄₅Te₀.₆₃Se₀.₃₄     | 3.7990 | 6.034⁴ | 3.00⁴    | <?           |
| 0.5 at.% of Ni | Fe₀.₉₅Ni₀.₀₅Te₀.₆₅Se₀.₃₄     | 3.8046 | 6.084⁹ | 5.70     | 11.7         |
| 1 at.% of Ni  | Fe₀.₉₄Ni₀.₀₆Te₀.₆₄Se₀.₃₅     | 3.803⁴ | 6.087₈ | 2.45     | 10.9         |
| 1.5 at.% of Ni| Fe₀.₉₃Ni₀.₀₇Te₀.₆₃Se₀.₃₅     | 3.801⁴ | 6.088₁ | 3.38     | 9.9          |
| 2 at.% of Ni  | Fe₀.₉₂Ni₀.₀₉Te₀.₆₂Se₀.₃₅     | 3.800⁶ | 6.087₅ | 1.9₇     | <?           |
| 5 at.% of Ni  | Fe₀.₉₀Ni₀.₁₃Te₀.₆₁Se₀.₃₅     | 3.800⁵ | 6.08₁₅ | 1.2₅     | <?           |
| 10 at.% of Ni | Fe₀.₈₅Ni₀.₁₇Te₀.₆ₐSe₀.₃₅     | 3.7₉₉₇ | 6.0₅₅₅ | 2.₅₅     | <?           |
| 20 at.% of Ni | Fe₀.₇₅Ni₀.₂₇Te₀.₅₉Se₀.₃₄     | 3.8₀₁₅ | 6.₀₂₈₈⁸ | 1.₇₃⁸ | <?           |
| 0.5 at.% of Cu | Fe₀.₉₅Cu₀.₀₅Te₀.₆₅Se₀.₃₄     | 3.₈₀₁₀ | 6.₀₉₁₁ | 1.₇₀     | 7.₆          |
| 1 at.% of Cu  | Fe₀.₉₄Cu₀.₀₇Te₀.₆₄Se₀.₃₅     | 3.₈₀₂₂ | 6.₀₈₆₅ | 1.₄₇     | <₃.₅         |
| 2 at.% of Cu  | Fe₀.₉₃Cu₀.₀₉Te₀.₆₃Se₀.₃₅     | 3.₈₀₂₆ | 6.₀₉₀₁ | 2.²₇     | <?           |
| 5 at.% of Cu  | Fe₀.₉₀Cu₀.₁₁Te₀.₆₂Se₀.₃₅     | 3.₈₀₁₇ | 6.₀₆₈₂ | 1.₉₂     | <?           |
| 10 at.% of Cu | Fe₀.₈₅Cu₀.₁₃Te₀.₆₧Se₀.₃₅     | 3.₈₀₀₈ | 6.₀₄₈₆ | 1.₃₅     | <?           |
| 20 at.% of Cu | Fe₀.₇₅Cu₀.₁₅Te₀.₆₉Se₀.₃₅     | 3.₈₀₀₃ | 6.₀₂₇₂⁸ | 1.₆₅⁶ | <?           |

<sup>a</sup> beginning of the crystal.
<sup>b</sup> end of the crystal.

3.3. The influence of chemical substitution on the superconducting transition temperature of FeTe₀.₆₅Se₀.₃₅ single crystals

The effect of chemical substitution at the Fe site on the superconducting transition temperature has been investigated...
and the temperature dependence of AC susceptibility has been measured for all of the studied crystals. Since the experimental set-up for crystallization is a closed system, all of the inclusions may affect the final product of the crystallization. In particular, the change of Se/Te ratio or iron content in the host lattice is expected for the dopants not incorporated into the FeTe$_{1-x}$Se$_x$ matrix when selenides, tellurides or binary metal compounds are formed. The concentration changes in the matrix are proportional to the amount of dopant added. When the addition of dopants leads to the creation of a metal selenide compound, the selenium content $x$ in the matrix decreases. In such a case, a decrease of $T_c$ is expected because of the relation between Se/Te ratio in the crystal and its $T_c$. We have found that it takes place in the samples doped with Mn and Mo. Nevertheless, the change of $T_c$ in the samples doped with Cd is negligible. For the samples doped with Ga and Hg, the slight increase of $T_c$ values was observed but these changes cannot be related with the changes in the ratio of Se/Te in the matrix (see table 3 with EDX data). This effect is not fully understood at the present and needs additional studies.

The decrease of $T_c$ with increasing Mn content for the samples doped with manganese is well visible in the magnetic susceptibility data (see figure 8).

The observed changes in $T_c$ are caused by a decrease of selenium content $x$ in the FeTe$_{1-x}$Se$_x$ matrix as estimated from EDX or x-ray measurements. It was found for the studied samples that the volume of nonsuperconducting phase increases with increasing dopant inclusion content since a weakening of the intensity of the diamagnetic signal was observed. The width of the transition to the superconducting state is correlated with the crystallographic quality of the crystal in the same way as was found for FeTe$_{1-x}$Se$_x$.

For the samples doped with cobalt, it was found that superconductivity is suppressed by 5 at.% Co substitution into Fe site in single crystals of FeTe$_{0.65}$Se$_{0.35}$ as well as of FeTe$_{0.5}$Se$_{0.5}$ (composition determined by EDX expressed as Fe$_{0.05}$Co$_{0.05}$Te$_{0.5}$Se$_{0.5}$ with $\Delta \omega = 0.95$ arc min). All of the single crystals substituted with over 5 at.% of Co or 2 at.% of Ni or Cu do not show superconductivity. Nevertheless, some traces of superconductivity are visible in AC susceptibility, most likely due to local inhomogeneity in Co distribution. In contrast, single crystals of Fe$_{0.935}$Co$_{0.065}$Te$_{0.65}$Se$_{0.35}$

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**Table 3.** Summary of the chemical composition of the matrix and inclusions for selected single crystals of FeTe$_{0.65}$Se$_{0.35}$ doped with the elements not incorporated into the host lattice.

| at.% of dopant | Matrix composition by EDX ($\pm 0.02$) | Inclusions |
|----------------|----------------------------------------|------------|
| 5 at.% of Zn   | Fe$_{0.17}$Te$_{0.65}$Se$_{0.31}$       | ZnSe       |
| 5 at.% of Mn   | Fe$_{0.17}$Te$_{0.65}$Se$_{0.31}$       | MnSe + (FeMn)$_2$O$_3$ |
| 20 at.% of Mn  | Fe$_{0.17}$Te$_{0.72}$Se$_{0.22}$       | MnSe + (FeMn)$_2$O$_3$ |
| 5 at.% of Cd   | Fe$_{0.13}$Te$_{0.66}$Se$_{0.34}$       | CdTe$_{1-x}$Se$_x$ |
| 2 at.% of In   | Fe$_{0.05}$Te$_{0.65}$Se$_{0.35}$       | In–Te      |
| 5 at.% of Mo   | Fe$_{0.15}$Te$_{0.77}$Se$_{0.22}$       | Mo(Se$_{0.5}$O$_{0.7}$)$_2$ + MoTe$_{0.5}$Se$_{0.6}$ |
| 2 at.% of Pb   | Fe$_{0.13}$Te$_{0.73}$Se$_{0.34}$       | Fe–Pb–Te  |
| 2 at.% of Hg   | Fe$_{0.13}$Te$_{0.65}$Se$_{0.33}$       | Fe–Hg–Te  |
| 5 at.% of V    | Fe$_{0.17}$Te$_{0.65}$Se$_{0.32}$       | V$_{0.65}$Fe$_{0.35}$ |
| 1 at.% of Ga   | Fe$_{0.07}$Te$_{0.65}$Se$_{0.34}$       | Fe$_{0.2}$Ga$_{0.8}$O   |
| 5 at.% of Mg   | Fe$_{0.13}$Te$_{0.65}$Se$_{0.34}$       | Mg$_{0.5}$Si$_{0.5}$Na:K:O |
| 1 at.% of Al   | Fe$_{0.13}$Te$_{0.65}$Se$_{0.34}$       | Precipitations with dopant elements on the top of the ingot |
| 5 at.% of Ti   | Fe$_{0.13}$Te$_{0.65}$Se$_{0.33}$       |             |
| 5 at.% of Cr   | Fe$_{0.13}$Te$_{0.65}$Se$_{0.34}$       |             |
| 1 at.% of Sr   | Fe$_{0.13}$Te$_{0.65}$Se$_{0.34}$       |             |
| 1 at.% of Nd   | Fe$_{0.13}$Te$_{0.65}$Se$_{0.33}$       |             |
Fe\textsubscript{0.985}Ni\textsubscript{0.015}Te\textsubscript{0.65}Se\textsubscript{0.35} and Fe\textsubscript{0.99}Cu\textsubscript{0.01}Te\textsubscript{0.65}Se\textsubscript{0.35} and those with lower concentrations of Co, Ni and Cu show superconductivity. Copper substitution is the most effective in the suppression of superconductivity while the impact of cobalt substitution is the smallest one, in good agreement with theoretical calculations [48, 49]. Temperature dependences of the real and imaginary part of AC magnetic susceptibility for Fe\textsubscript{1−y}Co\textsubscript{y}Te\textsubscript{0.65}Se\textsubscript{0.35} (0.005 < y < 0.045) single crystals are shown in figures 9–12. For all of the studied samples, critical temperature and superconducting volume fraction decrease with increasing dopant content. It seems that the recently described effect of iron excess on superconducting properties of the pure Fe–Te–Se system [23, 28, 34, 38, 49–53] is much smaller than the impact of the TM dopant, especially on the critical temperature value. However, taking into account that there is no simple relation between the Fe/TM (TM = Co, Ni or Cu) ratio sufficient to alter the compound from superconducting to nonsuperconducting it is not trivial at all to make any prediction about the necessary conditions for the substituted system to maintain superconductivity (for example, compare two samples substituted with 1% of Cu, see table 2).

4. Conclusions

Superconducting single crystal of pure Fe\textsubscript{Te\textsubscript{1−x}Se\textsubscript{x}} (x = 0.3–0.55) and Fe\textsubscript{Te\textsubscript{0.66}Se\textsubscript{0.34}) doped with Co, Ni, Cu, Mn, Zn, Mo, Cd, In, Pb, Hg, V, Ga, Mg, Al, Ti, Cr, Sr or Nd into Fe ion sites have been grown using Bridgman’s method. It has been found that the sharpness of the transition to the superconducting...
state in FeTe$_{1-x}$Se$_x$ is evidently inversely correlated with crystallographic quality of the crystals. Crystals with a higher value of FWHM exhibit a narrower transition to the superconducting state. As the $\Delta\omega$ value decreases, indicating a decrease of defect concentration, the width of the transition increases.

It has been found that, among examined substitutions of Fe site by Co, Ni, Cu, Mn, Zn, Mo, Cd, In, Pb, Hg, V, Ga, Mg, Al, Ti, Cr, Sr and Nd, only Co, Ni and Cu ions are incorporated at the Fe site into the host lattice of the FeTe$_{0.65}$Se$_{0.35}$ single crystals. All of the single crystals substituted with Co over 5 at.% and with Ni over 2 at.% as well as with Cu over 1.5 at.% are not superconducting. The crystals of Fe$_{0.95}$Co$_{0.05}$Te$_{0.65}$Se$_{0.35}$, Fe$_{0.98}$Ni$_{0.015}$Te$_{0.65}$Se$_{0.35}$ and Fe$_{0.99}$Cu$_{0.01}$Te$_{0.65}$Se$_{0.35}$ and those with lower concentrations of dopant exhibit superconductivity. The rest of the studied dopants do not incorporate into the host lattice of FeTe$_{0.65}$Se$_{0.35}$ single crystals. Inclusions, formed with elements not incorporated into the matrix, change the chemical composition of the crystals, leading to the changes in Se/Te ratio, which has an impact on the value of the critical temperature. The sharpening of transition to the superconducting state is strongly correlated with the crystallographic quality of the crystals, similarly as in the case of undoped crystals.

The small disorder introduced into the magnetic sublattice, by partial replacement of Fe ions with nonmagnetic ions of Cu or with magnetic ions of Ni or Co with spin values different from that of Fe ions, strongly suppresses superconductivity in the FeTe$_{1-x}$Se$_x$ system. It means that, even if superconductivity can appear in the system containing magnetic ions, it will not survive if the disorder in the magnetic ion sublattice is introduced, most likely because of magnetic scattering of Cooper pairs. This is an indication of the s-wave pairing in the superconducting Fe–Se–Te system.

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