I. INTRODUCTION

Iron chalcogenides, Fe$_{1+y}$Te$_2$Se$_{1-z}$ are promising candidates to understand the mechanism of superconductivity in the family of Fe-based superconductors owing to their archetypical binary atomic pattern. The tetragonal PbO-type Fe$_{1+y}$Se$_2$ with a superconducting transition temperature $T_c = 8$ K is the simplest member of Fe-based superconductors because of its structure and chemical composition. The structure comprises stacks of edge-sharing FeSe$_4$ tetrahedra, which form layers orthogonal to the c-axis. The homogeneity range of tetragonal Fe$_{1+y}$Se$_2$ is very narrow. The compound is nearly stoichiometric, and minute change in the composition controls the physical and low temperature structural properties. For example, Fe$_{1.01}$Se$_2$ is superconducting and the crystal structure transforms from a tetragonal ($P4/nmm$) to an orthorhombic ($Cmma$) phase at around 90 K, whereas non-superconducting Fe$_{1.03}$Se$_2$ does not exhibit this structural transition. The $T_c$ of Fe$_{1+y}$Se$_2$ can be enhanced up to 37 K by applying external pressure of 7−9 GPa or up to 15 K by about 50 % substitution of Te at ambient pressure. The bulk superconductivity disappears with higher Te substitution and the end member, Fe$_{1+y}$Te$_2$, is non-superconducting.

Fe$_{1+y}$Te$_2$ with an analogous crystal structure to Fe$_{1+y}$Se$_2$ occurs only in the presence of excess Fe, which is situated in the interstitial 2e crystallographic sites within the chalcogenide planes. Instead of superconductivity, tetragonal Fe$_{1+y}$Te$_2$ shows a complex interplay of magnetic and structural phase transitions in dependence of the excess amount of Fe$_{1+y}$Te. A simultaneous first-order magnetic and structural transition from the tetragonal paramagnetic to the monoclinic ($P2_1/m$) commensurate antiferromagnetic phase is observed at $T_s = 46$ K in Fe$_{1.06}$Te. The first-order transition temperature systematically decreases down to 57 K with an increase in $y$ from 0.06 to 0.11. For $y > 0.11$, two transitions are observed: in the specific case of $y = 0.13$, a continuous transition at 57 K and a first-order phase transition at lower temperature. This behavior suggests the presence of a tricritical point close to this composition. For larger amounts of interstitial Fe, $y = 0.15$, once again a single phase transition is observed at 63 K in the heat capacity measurements. However, this phase transition is a continuous (λ-like in specific heat) transition from tetragonal paramagnetic to orthorhombic incommensurate antiferromagnetic phase. The microscopic mechanisms driving these phase transitions are not yet well understood.

A strong influence of excess Fe on the magnetic and crystallographic properties of Fe$_{1+y}$Te$_2$ ($y = 0.076$, 0.141, and 0.165 ) was first reported by Bao et al. based on neutron diffraction experiments. Following this report, several other groups made similar observations. However, due to extreme sensitivity of the physical properties of Fe$_{1+y}$Te$_2$ to the amount of $y$, it is often difficult to compare the results of independent measurements. Furthermore, Rodriguez et al. reported a phase diagram of Fe$_{1+y}$Te$_2$ for FeTe in the nominal range 1.04−1.18:1, while a report by Mizuguchi et al. extended the phase diagram up to 1.3:1. These results suggest an ambiguity in the homogeneity range of the room temperature tetragonal phase of Fe$_{1+y}$Te$_2$. Therefore, our goal here is to establish the homogeneity range based on careful x-ray diffraction experiments and physical property measurements on chemically well characterized samples. In our previous study, we presented a tentative phase diagram of Fe$_{1+y}$Te$_2$, which is incomplete around the composition $y = 0.11$. In the case of Fe$_{1.13}$Te$_2$, we reported two thermodynamic anomalies, and assigned the phase transition at lower temperature $T_s = 46$ K to the structural transformation. However, a recent report on the same nominal composition by Mizuguchi et al. shows a two-step structural phase transition, from tetragonal−orthorhombic followed by orthorhombic−monoclinic structure upon cooling. Further, the neutron diffraction data on Fe$_{1.10}$Te$_2$ with similar thermodynamic properties like our Fe$_{1.13}$Te$_2$ indicated a structural anomaly at 63 K followed by a long-range
magnetic order at 57.5 K. These different results may also be related to subtle differences in the Fe content.\textsuperscript{13} Here, we focus on the detailed analysis of the powder diffraction patterns and the temperature dependence of the peak-width in Fe\textsubscript{1+y}Te within the range 0.11 ≤ y ≤ 0.15 to understand which phases are involved close to the tricritical point in the Fe\textsubscript{1+y}Te phase diagram. We aim to fill-in the gaps as well as revise the phase diagram to gain a clearer picture of the interplay between structure and magnetism in these compounds.

II. EXPERIMENTAL

Polycrystalline Fe\textsubscript{1+y}Te samples were synthesized utilizing the solid-state reaction method as described in Ref. 16 with different amounts of excess iron in the range 0.02 ≤ y ≤ 0.20. Prepared samples were investigated by x-ray powder diffraction (XRD) using Co K\textsubscript{α1} radiation (\(\lambda = 1.788965 \text{ Å}\)). The lattice parameters of samples were calculated with LaB\textsubscript{6} as an internal standard in the x-ray powder diffraction experiments. As the amount of excess iron is extremely important for the physical properties of Fe\textsubscript{1+y}Te, the synthesized phase-pure samples were characterized by wavelength dispersive x-ray (WDX) analysis and chemical analysis by an inductively coupled plasma method (ICP). In calculating the standard deviation of the nominal compositions mass loss after reaction was accounted for assuming that all loss is caused by tellurium evaporation. However, this error bar is smaller than the symbol size.

FIG. 1. X-ray diffraction diagram of samples with nominal composition Fe\textsubscript{1+y}Te for y = 0.04 – 0.17, tetragonal Fe\textsubscript{1+y}Te as the main phase at room temperature. (Impurity phases; FeTe\textsubscript{2} marked by • and elemental Fe by ♦) (b) Lattice parameters at room temperature in dependence of the nominal composition Fe\textsubscript{1+y}Te. The error bars here are smaller than the size of the symbols.

III. RESULTS AND DISCUSSION

The XRD patterns of Fe\textsubscript{1+y}Te (y = 0.04, 0.06, 0.08, 0.11, 0.13, 0.15, and 0.17) samples at ambient temperature are presented in Fig. 1 (a). FeTe\textsubscript{2} and Fe impu-
FIG. 3. Specific heat of Fe$_{1+y}$Te for $y = 0.11 - 0.15$. The $C_p(T)$ data for $y = 0.115 - 0.15$ are shifted by the amounts given for each curve for clarity. Arrows show the disappearing first-order phase transition upon increasing Fe composition.

Figures were observed in XRD patterns for compositions $y < 0.06$ and $y > 0.15$, respectively. Previously reported excess amount of iron in tetragonal Fe$_{1+y}$Te ranged from 0 to 30 %, 12,15,20–22 According to our x-ray diffraction study and lattice parameters represented in Figs. 1(a) and (b), the homogeneity range of tetragonal Fe$_{1+y}$Te is clearly smaller than those given in these previous reports. In Fig 2, the experimentally determined composition by WDX and ICP spectroscopic method are compared to the nominal composition. While the amount of Fe as obtained by the ICP method is systematically 1–2 % higher than the nominal composition, WDX analysis gives an amount of iron that is typically 1–3 % lower. The compositions obtained from WDX and chemical analysis overlap with the nominal composition within three standard deviations, 3σ.

The temperature dependence of the specific heat of Fe$_{1+y}$Te for $y = 0.11 - 0.15$ is presented in Fig. 3. For $y = 0.11$, a peak corresponding to a simultaneous first-order magnetic and structural phase transition at $\approx 58$ K is observed. With minute increase in the Fe composition, however, two phase transitions can be distinguished. Already for $y = 0.115$ these two transitions are well separated. For the composition Fe$_{1.12}$Te, the $\lambda$–like second order phase transition at 57 K is followed by a first-order phase transition at lower temperature, 46 K, as reported previously for a single crystal with nominal composition Fe$_{1.13}$Te. 24 With increasing Fe-content, the first-order phase transition at lower temperature disappears and for $y = 0.14$ only one transition is detected around 59 K with the characteristics of a continuous phase transition. The corresponding transition for $y = 0.15$ is found at a slightly increased temperature of 63 K.

In order to compare the crystallographic phase transition of Fe$_{1+y}$Te compositions to their magnetic and electrical properties, we performed magnetic susceptibility $\chi(T)$ and resistivity $\rho(T)$ measurements. Figs. 4(a)–4(e) display the temperature dependence of magnetic susceptibility measured under magnetic field of 0.1 T in field-cooling (FC) protocol for 0.11 ≤ $y$ ≤ 0.15. The magnitude of $\chi$ rises with increasing $y$ because excess Fe has a strong magnetic moment. 23 The transition temperatures obtained from specific heat and susceptibility measurements are in good agreement. The cooling and warming cycles in the susceptibility measurements exhibit a small thermal hysteresis for Fe$_{1.11}$Te, which is typical for a first-order phase transition (Fig. 4a). This thermal hysteresis in $\chi$ is broader for samples with $y = 0.12$ and 0.13 for which specific heat measurements indicated the presence of two consecutive phase transitions. For even higher values of $y$, cf. Figs. 4(d) and 4(e), there is no thermal hysteresis in magnetic susceptibility measurement. Such behavior is in accordance with what is expected for a continuous phase transition. Fig. 4(f) presents a summary of the temperature dependence of normalized resistance (R/R$_{300K}$) measured in the heating cycle. Similar
FIG. 5. Representative powder XRD patterns of Fe$_{1.11}$Te in the temperature regime 38 – 58 K for the (112) and (200) Bragg reflections. The green and red curves indicate an onset of orthorhombic and monoclinic distortions, respectively.

TABLE I. Parameters of crystal structures and refinements, atomic positions and atomic displacement parameters $U_{iso}$ (in $10^{-2}$ Å$^2$) for Fe$_{1.11}$Te at room temperature and 10 K.

| Temperature | 293 K | 10 K |
|-------------|-------|------|
| Space group | $P4/nmm$ | $P2_1/m$ |
| $a$ (Å)    | 3.8253(3) | 3.8368(8) |
| $b$ (Å)    | $a$ | 3.7873(8) |
| $c$ (Å)    | 6.27870(6) | 6.25409(13) |
| $\beta$ (deg.) | 90 | 90.668(1) |
| $R_I/R_P$  | 0.015/0.060 | 0.015/0.089 |
| Number of reflections | 81 | 323 |
| Refined parameters for profile/crystal structure | 21 / 5 | 30 / 10 |
| Atomic parameters | | |
| Fe1 | $2a (\frac{1}{2}, \frac{1}{2}, 0)$ | $2c (\frac{1}{2}, \frac{1}{2}, z)$ |
| | $x = 0.7368(4)$ | $z = 0.28207(5)$ |
| Fe2 | $2c (\frac{1}{2}, \frac{1}{2}, z)$ | $2c (x, \frac{1}{2}, \frac{1}{2}, z)$ |
| | $x = 0.7368(4)$ | $z = 0.28207(5)$ |
| Te | $U_{iso} = 0.83(2)$ | $U_{iso} = 0.68(3)$ |
| Occupancy | | |
| Fe1 | 0.108 (1) | 0.108(0) |
| Fe2 | $2c (\frac{1}{2}, \frac{1}{2}, z)$ | $2c (x, \frac{1}{2}, \frac{1}{2}, z)$ |
| | $x = 0.7368(4)$ | $z = 0.28207(5)$ |
| Te | $U_{iso} = 0.94(1)$ | $U_{iso} = 0.75(1)$ |

thermal hysteresis as seen in $\chi$ was observed in resistivity measurements for the same compositions (not shown here). Below the phase transition temperatures, Fe$_{1.11}$Te shows a metallic behavior, while samples with higher Fe content, $y \geq 0.14$, display increasing resistivity with decreasing temperature.
Rietveld refinement, the composition is determined as 

$$\text{Fe}_{1+y} \text{Te}$$

ature and 10 K are given in Fig. 6. According to the 

transformation from tetragonal (P4/nnm) to monoclinic (P2_1/m) 

peak splitting of both (200) and (112) Bragg 

in the temperature regime 38 K corresponds to an incomplete orthorhombic to mon-

otherhombic symmetry, the (112) peak does not exhibit 

variations of specific heat and synchrotron XRD measurements, the 

Te at room temperature and 10 K are given 

Te consists of a mixture of orthorhombic 

Fe_{1.11}Te are compiled in Table II. From the results 

Fe_{1.12}Te can only be fitted reason-

as a mixture of orthorhombic and monoclinic phases 

Fe_{1.12}Te at 70 K can be fitted reason-

at 10 K. According to Mizuguchi et al., the 

estimated population of orthorhombic phase at 5 K is 

20 – 30% which is close to our results at 10 K. The 

details of the refinement of Fe_{1.12}Te are compiled in Ta-

At higher Fe content, y = 0.14, the broadening of the 

(200) peak appears at 54 K and visible splitting is mon-

is sluggish because of a strong competition be-

The powder x-ray diffraction patterns of Fe_{1,12}Te at several temperatures were investigated by Rietveld re-

determine the crystal structure at different 

To correlate the physical properties with the crystal 

structures, we performed high-resolution synchrotron x-

ray diffraction of the polycrystalline samples from 70 to 

10 K with 2 K temperature intervals. A complete struc-

ture refinement was conducted for all studied composi-

tions. Fig. 5 represents the selected region of XRD pat-

tern for the (112) and (200) Bragg reflections of Fe_{1.11}Te in the temperature regime 38 – 58 K during the cooling cycle. The peak splitting of both (200) and (112) Bragg 

reflections is characteristic of the monoclinic (P2_1/m) phase transition in the Fe_{1+y}Te system. In Fig. 5, 

a broadening of the (200) reflection can be seen at 56 K, while the peak splits into (200) and (020) at 54 K. 

A broadening of the (112) reflection is visible at 52 K and the splitting into (112) and (-112) becomes more 

pronounced at lower temperatures. A full-profile refine-

ment of powder XRD data of Fe_{1.11}Te at room temperature and 10 K are given in Fig. 6. According to the 

Rietveld refinement, the composition is determined as 

Fe_{1.108(1)}Te, which is consistent with the nominal com-

position. The refined data confirm the temperature-induced transformation from tetragonal (P4/nnm at 293 K) to 

the monoclinic phase (P2_1/m at 10 K) at low temper-

ature. Refined parameters of the crystal structures are represented in Table I. Note that there is no indication 

for any presence of an orthorhombic phase in Fe_{1.11}Te at 10 K.

In the case of Fe_{1.12}Te with two distinct phase trans-

itions, the broadening of the (200) reflection starts at around 54 K and the splitting is visible at 50 K (Fig. 7(a)). However, for the (112) peak, no apparent change of the peak shape was observed down to 42 K, see Fig. 7(b). Below 42 K, the (112) peak starts broadening but no clear splitting is observed even at the base temperature, 10 K, in contrast to Fe_{1.11}Te. Our observations confirm that Fe_{1.12}Te consists of a mixture of orthorhombic (Pmmn) and monoclinic (P2_1/m) phases at low temperature, as reported by Rodriguez et al. From the results of specific heat and synchrotron XRD measurements, the 

λ–like second order phase transition at 57 K is associated with the structural phase transition from tetragonal to orthorhombic symmetry, while the first-order phase transition observed in the specific heat measurements at 46 K corresponds to an incomplete orthorhombic to mon-

oclinic phase transition. The latter phase transition in Fe_{1.12}Te is sluggish because of a strong competition be-

between orthorhombic and monoclinic phases.

The powder x-ray diffraction patterns of Fe_{1.12}Te at several temperatures were investigated by Rietveld re-

To correlate the physical properties with the crystal 

structures, we performed high-resolution synchrotron x-

ray diffraction of the polycrystalline samples from 70 to 

10 K with 2 K temperature intervals. A complete struc-

ture refinement was conducted for all studied composi-

tions. Fig. 5 represents the selected region of XRD pat-

tern for the (112) and (200) Bragg reflections of Fe_{1.11}Te in the temperature regime 38 – 58 K during the cooling cycle. The peak splitting of both (200) and (112) Bragg 

reflections is characteristic of the monoclinic (P2_1/m) phase transition in the Fe_{1+y}Te system. In Fig. 5, 

a broadening of the (200) reflection can be seen at 56 K, while the peak splits into (200) and (020) at 54 K. A broadening of the (112) reflection is visible at 52 K and the splitting into (112) and (-112) becomes more pronounced at lower temperatures. A full-profile refinement of powder XRD data of Fe_{1.11}Te at room temperature and 10 K are given in Fig. 6. According to the Rietveld refinement, the composition is determined as Fe_{1.108(1)}Te, which is consistent with the nominal composition. The refined data confirm the temperature-induced transformation from tetragonal (P4/nnm at 293 K) to the monoclinic phase (P2_1/m at 10 K) at low temper-
TABLE II. Parameters of crystal structures and refinements, atomic positions and atomic displacement parameters \( U_{\text{iso}} \) (in \( 10^{-2} \ \text{Å}^2 \)) for Fe\(_{1.12}\)Te in the tetragonal phase at 70 K and in the mixed phase at 10 K.

| Temperature | 70 K | 10 K | 10 K |
|-------------|------|------|------|
| Space group | \( P4/nmm \) | \( P2_1/m \) | \( P4/nmm \) |
| \( a \) (Å)  | 3.81200(5) | 3.83845(4) | 3.82971(1) |
| \( b \) (Å)  | = \( a \) | 3.78807(3) | 3.79463(1) |
| \( c \) (Å)  | 6.25119(9) | 6.25193(5) | 6.2521 (1) |
| \( \beta \) (deg.) | 90 | 90.649(1) | 90 |
| \( R_t/R_F \) | 0.013/0.084 | 0.013/0.054 | 0.008/0.054 |
| Number of reflections | 80 | 232 | 133 |
| Atomic parameters | | | |
| Fe\(_1\) | \( 2a \ (\frac{3}{4}, \frac{1}{2}, 0) \) | \( 2c(x, \frac{1}{2}, z) \) | \( 2b \ (\frac{3}{4}, \frac{1}{2}, z) \) |
| | \( x = 0.7378(3) \) | \( z = 0.0019(3) \) | \( z = 0.0042(7) \) |
| Fe\(_2\) | \( 2c \ (\frac{1}{4}, \frac{1}{2}, z) \) | \( 2c(x, \frac{1}{2}, z) \) | \( 2a \ (\frac{1}{4}, \frac{1}{2}, z) \) |
| | \( x = 0.258(3) \) | \( z = 0.714(2) \) | \( z = 0.745(3) \) |
| | \( U_{\text{iso}} = 0.3(0) \) | \( U_{\text{iso}} = 0.2(0) \) | \( U_{\text{iso}} = 0.2(0) \) |
| Te | \( 2c \ (\frac{1}{4}, \frac{1}{2}, z) \) | \( 2c \ (x, \frac{1}{2}, z) \) | \( 2c \ (x, \frac{1}{2}, z) \) |
| | \( x = 0.2432(2) \) | \( z = 0.2842(1) \) | \( z = 0.2805(3) \) |
| | \( U_{\text{iso}} = 0.3726(1) \) | \( U_{\text{iso}} = 0.2(0) \) | \( U_{\text{iso}} = 0.2(0) \) |

\( ^a \) For the refinement involving two phases, the occupancy of the Fe\(_2\) site was fixed at \( y = 0.12 \).

FIG. 9. Representative powder XRD patterns of Fe\(_{1.14}\)Te for the (112) and (200) Bragg reflections in the temperature regime 38 – 62 K. Broadening of the (200) peak sets in at 54 K (green line).

sum of the peak FWHM plus the separation of the peak maxima in case of visible splitting, i.e. a value which increases significantly upon peak splitting. In Fig. 11(a), the magnitude of FWHM of both (200) and (112) reflections in Fe\(_{1.11}\)Te starts to increase almost at the same temperature around 58 K. The difference of \( \approx 2 \) K between broadening of (200) and (112) peaks as mentioned earlier, is difficult to resolve in this analysis. However recent neutron diffraction measurements of Fe\(_{1.11}\)Te single crystals indicate an incommensurate antiferromagnetic precursor phase before a commensurate antiferromagnetic phase sets in. In contrast, the separation between transitions is much more pronounced for the composition Fe\(_{1.12}\)Te, see Fig. 11(b): The (200) reflection broadens at \( \approx 57 \) K whereas the value of FWHM of the (112) remains constant until 46 K. These temperatures are in conformity with the specific heat measurements. For Fe\(_{1.13}\)Te polycrystalline sample,(Fig. 11(c)) broadening in the (112) reflection is not as clear as for the previous compositions. Moreover there is a slight increase below 40 K, which coincides with the weak first-order phase transition monitored around the same temperature in specific heat. In Fig. 11(d), for \( y = 0.14 \), no change in the (112) reflections is observed while broadening in (200) reflections is quite obvious because of the transition into orthorhombic symmetry. But the changes in the FWHM values of the (200) reflections for both \( y = 0.14 \) and \( y = 0.15 \) (not shown) compositions were observed at \( 3 – 4 \) K lower than the corresponding antiferromagnetic ordering temperature \( T_N \). The FWHM analyses, in general, show that the onset temperatures of the phase transitions determined by heat capacity measurements are in conformity with the results of synchrotron XRD measurements.

In Figs. 12(a) and (b), the selected region of XRD patterns for (112) and (200) Bragg reflections of Fe\(_{1+y}\)Te,
FIG. 10. Refined synchrotron powder x-ray diffraction patterns of Fe$_{1.15}$Te at 293 K and 10 K.

FIG. 11. Temperature dependence of powder x-ray diffraction peaks of Fe$_{1+y}$Te, $y = 0.11 - 0.14$. (a-c) The broadening of the reflections (112) and (200) demonstrate a monoclinic distortion at low temperatures, whereas in (d) constant values for (112) indicate an orthorhombic low-temperature phase. Dashed lines in (b) were drawn to mark the temperatures at which phase transitions occur in the thermodynamic measurements.

FIG. 12. Representative powder XRD patterns of Fe$_{1+y}$Te, $y = 0.11 - 0.15$ at 10 K (a) and 30 K (b). For $y = 0.11$, both (200) and (112) peaks are clearly split at low temperatures confirming the monoclinic structure. The partially split (112) peak in the case of $y = 0.12$ sample shows that the compound is a mixture of orthorhombic and monoclinic phases at 10 K. The unsplit (112) peak at 10 K for $y = 0.14$ and $y = 0.15$ samples confirm pure orthorhombic phase at 10 K.

Our results on Fe$_{1.12}$Te are supporting the idea of a two-step evolution of the crystal structure from tetragonal via orthorhombic to monoclinic structures as suggested by Mizuguchi et al. In our previous report on Fe$_{1.13}$Te single crystals, only one structural phase transition was identified within the magnetically ordered phase. In any case, the present detailed investigations suggest that the low-temperature transition from orthorhombic to monoclinic phase is incomplete even at 10 K for these compositions. According to Martinelli et al. and our results, for lower Fe content, $y < 0.11$, the phase transition from tetragonal to monoclinic does not need an intermediate phase (orthorhombic) formation. But in the vicinity of a tricritical point on the right-hand side, the intermediate orthorhombic phase partially transforms towards monoclinic symmetry.

For a comparison of the metrical changes, the temperature dependence of the lattice parameters obtained from the refinements of several compositions $0.11 \leq y \leq 0.15$ during the cooling cycle are summarized in Figs. 13(a)–13(h). The splitting of lattice parameter $a$ at

$y = 0.11 - 0.15$, are given at 10 K and 30 K to summarize the low-temperature behaviors of different compositions. Fig. 12(b) exhibits that the samples Fe$_{1+y}$Te with $y \geq 0.14$ are clearly orthorhombic while Fe$_{1.14}$Te is in monoclinic phase already at 30 K. On the other hand, Fe$_{1.12}$Te at 30 K seems to be mostly in the orthorhombic phase because the peak splitting in (112) is not significant. At 10 K, the peak is broader but still there is not a clear splitting as a result of the mixture of orthorhombic and monoclinic phases.

The unsplit (112) peak at 10 K for Fe$_{1.14}$Te at temperatures above (293 K) and below (10 K) $y \leq 0.11$, both Fe$_{1.15}$Te and Fe$_{1.14}$Te at 30 K seem to be mostly in the orthorhombic phase, whereas Fe$_{1.12}$Te is confirmed to be pure orthorhombic at 10 K. For a comparison of the metrical changes, the temperature dependence of the lattice parameters obtained from the refinements of several compositions $0.11 \leq y \leq 0.15$ during the cooling cycle are summarized in Figs. 13(a)–13(h). The splitting of lattice parameter $a$ at
around $T_N$ is quite dramatic but remains almost constant throughout the monoclinic phase. In the orthorhombic phase, the difference between lattice parameters $a$ and $b$ is significantly smaller. The difference between the first-order and second-order phase transitions can be clearly seen in the $c$ parameters: For the monoclinic phase transition the increase of the $c$ parameter is sudden at around $T_N$ (Fig. 13(b)), whereas for the orthorhombic phase transition it changes smoothly (see Figs. 13(f) and (h)). The diffraction patterns of Fe$_{1.11}$Te can be refined as either purely orthorhombic or purely monoclinic phase down to 54 K without a significant difference in the residuals and lattice parameters. In Figs. 13(a) and 13(b), the overlap of lattice parameters for both phases can be seen between 60 and 54 K. Between 46 – 54 K, the lattice parameters of Fe$_{1.12}$Te were refined as orthorhombic phase. Below 46 K the lattice parameters were calculated assuming only a monoclinic phase for simplicity. Yet, even when the diffraction pattern were refined allowing for a mixture of two phases, the lattice parameters of the monoclinic structure did not exhibit a significant difference compared to fitting a purely monoclinic phase. In Fig. 13 (c) and (d) however, we show the lattice parameters of only monoclinic phase for clarity.

On the basis of our results, we propose a revised temperature-composition phase diagram of Fe$_{1+y}$Te. AFM and IC AFM stand for antiferromagnetic and incommensurate antiferromagnetic phase, respectively.

$$\text{TABLE III. Parameters of crystal structures and refinements, atomic positions and atomic displacement parameters } U_{\text{iso}} \text{ (in } 10^{-2} \text{ Å}^2) \text{ for Fe}_{1.15}\text{Te at room temperature and 10 K.}$$

| Temperature | 293 K | 10 K |
|-------------|-------|------|
| Space group | $P4/nmm$ | $Pmmn$ |
| $a$ (Å)     | 3.82835(2) | 3.81971(3) |
| $b$ (Å)     | $a$ | 3.79288(3) |
| $c$ (Å)     | 6.27019(4) | 6.25288(5) |
| $\beta$ (deg.) | 90 | 90 |
| $R_1/R_P$   | 0.022/0.067 | 0.021/0.073 |
| Number of reflections | 152 | 133 |
| Refined parameters for profile/crystal structure | 22 / 5 | 24/ 7 |
| Atomic parameters | | |
| Fe1         | $2a \left( \frac{1}{2}, \frac{1}{2}, 0 \right) \quad 2b \left( \frac{1}{2}, \frac{1}{2}, z \right)$ | $z = 0.0020(2)$ |
| Fe2         | $2c \left( \frac{1}{2}, \frac{1}{2}, z \right) \quad 2a \left( \frac{1}{2}, \frac{1}{2}, z \right)$ | $z = 0.7175(5) \quad z = 0.7159(8)$ |
| Occupancy   | 0.152 (1) | 0.152 |
| Te          | $2c \left( \frac{1}{2}, \frac{1}{2}, z \right) \quad 2a \left( \frac{1}{2}, \frac{1}{2}, z \right)$ | $z = 0.28400(3) \quad z = 0.28490(5)$ |
| $U_{\text{iso}}$ | 1.09(1) | 0.54(1)|
| $U_{\text{iso}}$ | 0.80(7) | 0.5(1) |

FIG. 13. Temperature dependence of lattice parameters $a$, $b$ and $c$ at various compositions. (a)-(d) Transition from tetragonal to monoclinic symmetry (with intermediate orthorhombic phase, represented by half full symbols) for $y = 0.11$ and 0.12. (e)-(g) Orthorhombic phase transition for $y = 0.14$ and 0.15. Below 46 K Fe$_{1.12}$Te consists of a mixture of orthorhombic and monoclinic phases. In (c) and (d), the lattice parameters below 46 K were evaluated assuming only a monoclinic structure exclusively.

FIG. 14. Revised temperature-composition phase diagram of Fe$_{1+y}$Te. AFM and IC AFM stand for antiferromagnetic and incommensurate antiferromagnetic phase, respectively.
paramagnetic tetragonal phase transforms into monoclinic commensurate antiferromagnetic phase without an intermediate phase formation while $T_N$ decreases from 69 K to 58 K with increasing Fe amount (as suggested in Ref. 14). A tricritical point is situated close to the composition $y \approx 0.11$ in the phase diagram. At composition, $y = 0.115$, a two-step phase evolution is apparent. At 10 K, for $0.115 \leq y \leq 0.13$, the materials are composed of a mixture of monoclinic and orthorhombic phases. The temperature difference between these transitions becomes more distinct upon increasing Fe amount. For $y > 0.13$, the phase transition from orthorhombic to monoclinic structure at lower temperature disappears and only single phase transition is observed. The latter is a second order phase transition from the tetragonal paramagnetic to orthorhombic incommensurate antiferromagnetic structure, which is in accordance with the neutron scattering experiments. However, the mysterious disappearance of the first order phase transition for $y > 0.13$ requires more closer examination.

IV. CONCLUSIONS

We provide a reference data base for cross-comparing different reports on Fe$_{1+y}$Te by conducting low-temperature synchrotron x-ray diffraction experiments, thermodynamic and resistivity measurements on a single series of chemically well-characterized samples. Based on these data we presented a revised phase diagram for Fe$_{1+y}$Te. A closer examination suggests a region of orthorhombic crystal symmetry for $y > 0.13$. Further, for $0.11 < y \leq 0.13$ the transition into orthorhombic crystal symmetry is followed by a two phase region at even lower temperature where also a monoclinic phase is found. Along with coinciding magnetic and structural phase transitions for $y < 0.11$, a two-step phase transition for $0.11 \leq y \leq 0.13$ was observed with both phase transitions having magnetic and structural components. This behavior indicates a strong magneto-elastic coupling in this system. However, details of the microscopic couplings and the origin of this complex interplay of magnetic and structural transitions in dependence of the Fe-content is yet to be explored.

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