The effect of sorption of air and hydrogen components on the structural characteristics of superconducting FeTe_{0.65}Se_{0.35} single crystals

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ABSTRACT

X-ray studies of iron chalcogenide $FeTe_{0.65}Se_{0.35}$ single crystals were performed after they were exposed in air and hydrogen atmospheres at room and high temperatures, for long periods of time. It is found that impurity components have a significant effect on the structural characteristics of the diffraction pattern for this layered tetragonal superconducting material. It is shown that molecular impurities do not change the matrix symmetry of the tetragonal substitution solutions. However, when hydrogen molecules dissociate close to 200 °C under the thermocatalytic effect of Fe atoms, the tetragonal lattice of the matrix becomes unstable. Symmetry is reduced against the background of an increased concentration of atomic hydrogen and strengthening of the chemical bonds in the crystals. The crystal density sharply increases, and a FeTe_{0.65}Se_{0.35} + H interstitial solution based on an orthorhombic lattice is formed. It is shown that the structural tetra-ortho phase transition in such solutions occurs near 200 °C.

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1. INTRODUCTION

FeTe_{0.65}Se_{0.35} single crystals are one of the new layered iron chalcogenides. They exhibit superconducting properties at temperatures below 14-16 K.1-4 This compound was first derived and intensively studied after superconductivity was discovered at 8 K in iron-containing FeSe crystals⁵ in 2008. The significant contrast between the critical temperatures of the substances in this class is apparently determined by the differences in how these compounds are acted upon, one such method involving the introduction of an atomic impurity, such as tellurium that partially replaces selenium, into the initial substance. In addition to creating substitution solutions based on FeSe,⁶ and other FeSe_{0.93}S_{0.07} and FeS chalcogenides with similar properties, the possibility of forming equilibrium interstitial solutions during intercalation into crystals, especially of hydrogen molecules, has recently been demonstrated. As a result of this action on $\text{FeSe}_{0.93}\text{S}_{0.07}$, it has been possible to increase the superconducting transition temperature by almost five times, from 9 to 42.5 K.⁷ This can be explained by the fact that under certain external conditions (temperature, pressure, medium, impurity concentration, etc.) the H₂ molecules dissociate, and its H ions enter into chemical interaction with the atoms of the original

substance. At the same time, the additional chemical pressure in the crystals acting in conjunction with external pressure, makes it possible to significantly affect the electrical and structural characteristics of the matrix. In the optimistic scenario, we assume that studies of iron-containing layered magnets with molecular and atomic hydrogen impurities will make it possible to obtain new data that will clarify the nature of the superconductivity in these solutions. As a first step, this study aims to shed light on the effect that hydrogen and other molecular impurities (air components, in particular) have on the structural and superconducting characteristics of FeTe_{0.65}Se_{0.35}.

2. SAMPLES AND EXPERIMENTAL PROCEDURE

FeTe_{0.65}Se_{0.35} single crystal samples with a good cut and high quality were grown from a melt using the Bridgman method at a rate of 1 mm/h. The crystals usually grow in the shape of flat plates with mean dimensions of $4 \times 5 \times 1$ mm, and have a tetragonal lattice with *P4/nmm* symmetry and parameters a = b = 3.799 Å, c = 6.093 Å, and V = 87.9 Å.² The crystal lattice structure of pure FeTe_{0.65}Se_{0.35} is studied in Ref. 8 and is diagrammed in Fig. 1.



FIG. 1. The structure of a layered α -Fe (Te, Se) crystal with tetragonal symmetry P4/nmm.⁸

The saturation of FeTe_{0.65}Se_{0.35} single crystals with air and hydrogen components was performed at several temperatures, pressures, and gas exposure times. The temperature varied from room temperature of 20 °C up to 250 °C, the pressure ranged from 10^{-3} mmHg to 5 atm, and the exposure time was as long as 720 h in some experiments (see Sec. 3 for more details). The structural studies were conducted using the DRON-3 polycrystalline X-ray

diffractometer in Cu–K_α copper anode radiation with $\lambda = 1.54178$ Å. At the same time, the β-radiation of the X-ray tube was significantly weakened by the corresponding Ni filter. The X-ray diffraction patterns of samples at room temperature were obtained by using the standard GP-15 attachment. The tetragonal single crystal samples at room temperature were oriented relative to the X-ray beam such that reliable data from the basal planes (001) could be obtained.

The experimental sequence was as follows. First, the X-ray diffraction pattern of the sample's initial state (Fig. 2) was obtained, since after it was grown the crystal was exposed to air for about a month before its exposure to hydrogen.

Then, in order to remove the air components that were "trapped" by the single crystal during growth and aging, and to decrease the level of internal stresses, the sample was vacuumized in a stainless steel chamber to pressures of 10^{-3} mmHg for ~ 200 h. Next, the crystal was removed from the chamber, X-rays were taken, and then it was mechanically cleaved along one of the planes. The X-rays were taken with respect to the (001) planes of the fresh chips, loosely coupled by van der Waals forces. The subsequent X-ray analysis of the newly cleaved crystal made it possible to obtain data for a pure crystal with no impurities. In the next step, single crystal samples were subjected to prolonged hydrogen exposure at various temperatures and gas pressures.

3. RESULTS AND DISCUSSION

Figure 3 shows the crystal's X-ray for the first diffraction line, obtained according to the procedure specified above, after exposure to molecular hydrogen at 20 °C.

A comparison of diffraction patterns (1) and (2) shows that evacuating the samples results in a noticeable weakening of the



FIG. 2. A typical X-ray diffraction pattern of the initial FeTe_{0.65}Se_{0.35} single crystal with tetragonal symmetry. Prior to image capture, the sample was exposed to air for more than a month at ordinary pressure and room temperature. The X-ray pattern was obtained by diffracting Cu– K_{α} radiation on the basal planes (001) at 20 °C.



FIG. 3. Changes to the structural characteristics of the first diffraction line (001) of $FeTe_{0.65}Se_{0.35}$ crystals, obtained for the initial state after prolonged exposure to air (1), subsequent vacuumization for two weeks at room temperature (2), for a pure crystal after cleaving along the basal plane (3), after exposing the crystal to hydrogen at a pressure of 2 atm and temperature of 20 °C for 48 h (4), and the same after a holding for 192 h (5).

diffraction pattern intensity, and its shift toward small-angle X-ray scattering. The latter points to an increase in the interplanar distances d_{001} and parameter c of the compound's tetragonal lattice. Diffraction pattern (3) shows that cleaving the crystal results in a sharp difference between (1) and (2). The intensity of the X-ray reflection from the (001) plane of the fresh cleavage almost tripled, its half-width decreased considerably, and it unexpectedly shifted toward larger diffraction angles. Exposure to molecular hydrogen H₂ at room temperature results in a small decrease in the intensity of reflections from the cleavage (001) planes, and their slight shift toward larger angles. The observed changes in the diffraction pattern are most likely caused by the intercalation of H₂ molecules into the interplanar spaces (the physical sorption effect). As a result of the averaged atomic-molecular interaction in such a solid solution, the diffraction intensity from the basal planes and the interplanar distances d_{001} tend to decrease, which also reduces parameter c. It is necessary to note that, according to our experimental data, the tetragonal structure of the crystals is retained.

Further experiments with hydrogen revealed that heating FeTe_{0.65}Se_{0.35} crystals even to the rather low temperature of $T \ge 200$ °C in a hydrogen environment at a pressure of 5 atm results in the formation of a qualitatively new diffraction pattern. The X-ray diffraction patterns display a rather intense asymmetric maximum (Fig. 4) at reflection angles $2\theta \sim 24-26^\circ$.

At the same time, the intensity and angular location of the reflections from the basal planes (001) are slightly changed. We made the assumption that the observed change in the diffraction pattern is caused by the structural phase transition of the lattice from tetragonal to orthorhombic. The transition is initiated by the thermocatalytic dissociation of H2 molecules, and by the filling of the interatomic vacancies in the basal planes by atomic hydrogen. According to the data from Ref. 9, such a process is quite possible in the system under study. The dissociation of hydrogen molecules occurs at the catalytically active centers of metals in the iron group at T > 200 °C.⁹ Therefore, as mentioned in Sec. 2, the FeTe_{0.65}Se_{0.35} crystals were heated in a hydrogen environment inside a reaction chamber that was made of stainless steel containing atoms of Fe, Ni, Co, and other elements. In addition, it is possible that the Fe atoms in the interlayers of the FeTe_{0.65}Se_{0.35} crystal will act as catalytic centers at increased temperatures, and reinforce both the cumulative effect of the H₂ molecules' dissociation and the chemical interaction between the hydrogen atoms and the atoms in the basal planes of the test compound. The presence of atomic hydrogen in the basal planes can significantly impact the interatomic interaction, reinforce its anisotropy and, as we observed, reduce the symmetry of the crystal structure from tetragonal to orthorhombic. According to our observations, this structural transition is accompanied by a significant jump in volume (see further) and by strong crystal distortions, the relaxation of which is expressed by the appearance of "waviness" in the form of macro-roughness on the cleaved planes. The effect of reducing the perfection of the FeTe_{0.65}Se_{0.35} crystals made it possible for us to observe the (010) and (100) reflections of the orthorhombic structure [Fig. 4(a)], along with the (001) reflections from the basal planes. As a result of analyzing the intensity of the additional asymmetric peak, it has been shown that it corresponds to the total intensity of the two (010) and (100) reflections [Fig. 4(b)] of the orthorhombic lattice with parameters a = 3.5437 Å, b = 3.5873 Å,



FIG. 4. A typical X-ray diffraction pattern of a FeTe_{0.65}Se_{0.35} single crystal with orthorhombic symmetry, obtained after its saturation by atomic hydrogen at 200 °C, is presented in Fig. 4(a). The observed weak reflections correspond to diffraction from the utilized copper substrate, and diffraction of the sample by X-ray β -radiation that was not entirely absorbed by the Ni filter. Figure 4(b) show the results of analyzing the intensity of the asymmetric reflection from the FeTe_{0.65}Se_{0.35} crystals.

c = 6.0763 Å, V = 77.3 Å³ ($\delta V/V = 13.76\%$), where V is the initial volume of the unit cell of a crystal, and δV is the change in the volume of the cell. The orthorhombic lattice parameters that have been presented correspond to samples maintained in a hydrogen atmosphere at 5 atm and 200 °C for 5 h. As the exposure time increases to 10 h, the reflection doublet is shifted to greater angles (see Fig. 5), its total intensity noticeably increases, and the lattice parameters acquire values equal to a = 3.5455 Å, b = 3.5835 Å, c = 6.0746 Å, and V = 77.2 Å³ ($\delta V/V = 13.8\%$).

It has been established that a further increase in the reaction chamber temperature to 250 °C also leads to increased crystal density due to changes in the orthorhombic lattice parameters to a = 3.4928 Å, b = 3.4505 Å, c = 6.0793 Å, and V = 73.27 Å³ ($\delta V/V = 14.6\%$) after a 5 h exposure to a hydrogen atmosphere at 5 atm. This temperature



FIG. 5. The effect of hydrogen exposure on the structural parameters of the total diffraction doublet for the (100) and (010) reflections of $FeTe_{0.65}Se_{0.35}$ crystals, at 200 °C and a hydrogen pressure of 5 atm.

resulted in an intense increase in stresses, an increased number of "rough" steps, and finally the destruction of the crystals, mainly due to delamination along the cleavage (001) planes. At the same time, the difference in the volumes of the tetragonal and orthorhombic lattices, as is clear from the values presented above, reaches nearly 15%.

Analysis of the diffraction patterns belonging to $FeTe_{0.65}Se_{0.35}$ single crystals intercalated by air, H₂, and hydrogen atom impurities showed that they all contain a wide diffuse halo with a maximum near $2\theta \approx 20^{\circ}$ (Fig. 6), which shifts slightly to small diffraction angles



FIG. 6. Changes in the background intensity of diffuse X-ray scattering on a $\text{FeTe}_{0.65}\text{Se}_{0.35}$ single crystal, with long-term exposure to vacuum (1), air (2), H₂ atmosphere at P = 2 atm and T = 20 °C (3), and also hydrogen environment at P = 5 atm and T = 200 °C (4), where there is thermocatalytic dissociation of H₂ molecules.

with a simultaneous increase in the integrated intensity relative to the crystal that went through vacuum cleaning [Fig. 6(1)].

Figures 7-9 show how different conditions (temperature, number of molecular and atomic impurities, impurity diffusion time, etc.) impact the structural characteristics (interplanar distances d_{001} , intensity, half-width X-ray diffraction reflections) of FeTe_{0.65}Se_{0.35} single crystals. It can be seen that the biggest impact comes from long-term exposure to air at room temperature, and subsequent vacuum treatment. At the same time, there is a significant increase in the interplanar distances, and a decrease of the intensity of diffraction reflections (001). If, in the first case, the increase in d_{001} can be explained by the number of molecules in the interplanar space of the layered tetragonal compound lattice, then it seems to us that in the second case, the effect of crystal "swelling" in vacuum does not have a simple, reasonable explanation without additional experiments. In this regard, it should be noted that a similar effect was observed in Ref. 10 during vacuum annealing of a related $Fe_{1.01}Te_{0.56}Se_{0.45}$ compound at 400 °C for a week (see Fig. 7). Unfortunately, the authors of Ref. 10 do not provide their own explanation of this phenomenon. In the same study, polycrystalline samples were also annealed in air at 270 °C but, evidently, because of the short exposure time (2 h) there were no observed changes in d_{001} . At the same time, the observed satisfactory agreement between the d_{001} values we obtained and those in Ref. 10, confirms the earlier conclusion that the X-ray



FIG. 7. How different conditions impact the interplanar distances d_{001} of a layered FeTe_{0.65}Se_{0.35} single crystal with tetragonal and orthorhombic symmetry: exposing the crystal to air for one month at room temperature, after it was grown (1); evacuating the crystal and storing it in a vacuum chamber for a month (2); X-ray diffraction of a fresh chip of the crystal obtained by cleaving along the (001) plane (3); X-ray diffraction of the crystal chip plane after 48 h of saturation with H₂ molecules at $P(H_{2}) = 2$ atm and T = 20 °C (4); after exposing the crystals for 5 (5) and 10 (6) hours, respectively, at $P(H_{2}) = 5$ atm and T = 200 °C; the same as (5), but at T = 250 °C (7). The data from Ref. 10 on interplanar distances for polycrystalline tetragonal samples of stoichiometrically similar Fe_{1.01}Te_{0.56}Se_{0.44} are presented for comparison : freshly grown sample (\blacktriangle), annealed for 2 h in air at 270 °C (∇) and annealed for 7 days in vacuum at 400 °C (\Box).



FIG. 8. How different conditions impact the reflection intensity of a layered FeTe_{0.65}Se_{0.35} single crystal with tetragonal and orthorhombic symmetry: exposing the crystal to air for one month at room temperature, after it was grown (1); evacuating the crystal and storing it in a vacuum chamber for a month (2); X-ray diffraction of a fresh chip of the crystal obtained by cleaving along the (001) plane (3); X-ray diffraction of the crystal chip plane after 48 (4), 192 (5), 336 (6) and 382 (7) hours of H₂ molecule saturation at $P(H_2) = 2$ atm and T = 20 °C; X-ray diffraction after exposing the crystals to a hydrogen medium at $P(H_2) = 5$ atm and T = 200 °C for 5 (8) and 10 (9) hours; same as (8), but at T = 250 °C (10).



FIG. 9. How different conditions impact the full width at half maximum (FWHM) of X-ray (001) reflection from a layered FeTe_{0.65}Se_{0.35} single crystal with tetragonal and (1–7) and orthorhombic (8–10) symmetry: exposing the crystal to air for one month at room temperature, after it was grown (1); evacuating the crystal and storing it in a vacuum chamber for a month (2); X-ray diffraction of a fresh chip of the crystal chip plane after 48 (4), 192 (5), 336 (6) and 382 (7) hours of H₂ molecule saturation at $P(H_2) = 2$ atm and T = 20 °C; X-ray diffraction after exposing the crystals to a hydrogen medium at $P(H_2) = 5$ atm and T = 200 °C for 5 (8) and 10 (9) hours; same as (8), but at T = 250 °C (10).

diffraction of fresh chips is equivalent to studying newly grown single crystals.

4. CONCLUSION

It follows from the obtained results that in studying the physical properties of iron chalcogenides, it is necessary to account for their high sensitivity to molecular air and hydrogen impurities, even at room temperatures. At increased temperatures (hundreds of degrees Celsius), the solubility of these substances can increase significantly, due to molecule dissociation on catalytically active Fe atoms that are structurally embedded into the layered lattice of this compound, and contained in the metal elements of the reaction chamber. Because the above-specified impurity molecules and atoms are present in the crystal, its structure is strongly distorted, and there is an increased concentration of local imperfections and internal stresses. A critical level of stresses and defects is attained at a particular temperature and concentration of atomic hydrogen in the compound, at which point the symmetry of the crystals is reduced, and there is a structural phase transition from a tetragonal to an orthorhombic crystal lattice. The phase transition established by us occurs only in interstitial solutions of hydrogen atoms, whereas the molecular components of air in the compositionallysimilar Fe_{1.01}Te_{0.56}Se_{0.44} do not change the symmetry of the lattice when heated to 270 °C.¹⁰ There is also no change in the lattice type upon heating in vacuum to 400 °C10 which indicates that the observed phase transition is likely chemical in nature, as opposed to thermal. Along with the structural changes in the crystalline phase, there was an observed accumulation of an amorphous state (Fig. 6) that manifested itself in the presence and growth of a diffuse halo as the temperature and solid solution formation time increased. Moreover, at low temperatures (T = 20 °C) the H₂ molecular impurity predominantly fills the space between the closely packed (001) layers and has a relatively weak effect on the interplanar, and especially intraplanar interaction between the compound elements (see Figs. 7 and 8). At higher temperatures $T \ge 200$ °C, where hydrogen transitions to the atomic state due to the thermocatalytic reaction, the effect of the hydrogen impurity becomes radical because the H ions have a chemical interaction with the compound atoms in the close-packed basal planes. This, evidently, results in additional partial amorphization of the FeTe_{0.65}Se_{0.35} crystal structure, causing an increase in the intensity of the diffuse halo (Fig. 6).

Structural studies of hydrogen intercalation of the FeTe_{0.65}Se_{0.35} single crystal suggest that it does not have to noticeably affect the superconducting properties of this compound after molecular hydrogen diffusion at room temperature. In contrast, intercalation by atomic hydrogen, which leads to a structural transition at 200–250 °C and a strong (by 15%) decrease (compression) of the crystal lattice cell volume, must cause a significant change in the electron-phonon interaction and, as a result, a significant change in the superconducting properties of the compound. Studies of these changes are planned for the near future.

REFERENCES

¹D. J. Gawryluk, J. Fink-Finowiski, A. Wiśniewski, R. Puzniak, V. Domukhovski, R. Deduszko, M. Kozlowski, and M. Berkowski, Supercond Sci. Technol. **24**, 065011 (2011).

²A. G. Sivakov, S. I. Bondarenko, A. I. Prokhvatilov, V. P. Timofeev, A. S. Pokhila, V. P. Koverya, I. S. Dudar, S. I. Link, I. V. Legchenkova, A. N. Bludov, V. Y. Monarcha, D. J. Gawryluk, J. Pietosa, M. Berkowski, R. Diduszko, R. Puzniak, and A. Wisniewski, Supercond Sci. Technol. **30**, 015018 (2017).

³S. I. Bondarenko, A. N. Bludov, A. Vishnevsky, D. Gavrilyuk, I. S. Dudar', V. P. Koverya, V. Y. Monarkha, A. G. Sivakov, and V. P. Timofeev, FNT **41**, 1148 (2015) [Low Temp. Phys. **41**, 897 (2015)].

⁴S. I. Bondarenko, A. N. Bludov, V. P. Koverya, S. I. Link, A. G. Sivakov, V. P. Timofeev, D. J. Gawryluk, R. Puzniak, and A. Wisniewski, Fiz. Nizk. Temp. 43, 1482 (2017) [Low Temp. Phys. 43, 1181 (2017)].

⁵F. C. Hsu, J. Y. Luo, K. W. Yeh, T. K. Chen, T. W. Huang, P. M. Wu, Y. C. Lee, Y. L. Huang, Y. Y. Chu, D. C. Yan, and M. K. Wu, Proc. Natl. Acad. Sci. 105, 14262 (2008).

⁶G. S. Burkhanov, S. A. Lachenkov, M. A. Kononov, B. A. Vlasenko, A. B. Mikhailova, and N. L. Korenovsky, Perspektivnye materialy 1, 54 (2017) [Inorg. Mater. Appl. Res. 8, 759 (2017)]. ⁷Y. Cui, G. Zhang, H. Li, H. Lin, X. Zhu, H.-H. Wen, G. Wang, J. Sun, M. Ma, Y. Li, D. Gong, T. Xie, Y. Gu, S. Li, H. Luo, P. Yu, and W. Yu, Sci. Bull. **63**, 11 (2018).

⁸W. Bao, Y. Qiu, Q. Huang, M. A. Green, P. Zajdel, M. R. Fitzsimmons, M. Zhernenkov, S. Chang, M. Fang, B. Qian, E. K. Vehstedt, J. Yang, H. M. Pham, L. Spinu, and Z. Q. Mao, Phys. Rev. Lett. **102**, 247001 (2009).

⁹K. A. Yagotintsev, I. V. Legchenkova, Y. E. Stetsenko, P. V. Zinov'ev, V. N. Zoryansky, A. I. Prokhvatilov, and M. A. Strzhemechny, FNT **38**, 1202 (2012) [Low Temp. Phys. **38**, 952 (2012)].

¹⁰C. Dong, H. Wang, Z. Li, J. Chen, H. Q. Yuan, and M. Fang, Phys. Rev. B 84, 224506 (2011).

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