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 FeSe\(_{0.93}S_{0.07}\), 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 H\(_2\) 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 × 5 × 1 mm, and have a tetragonal lattice with P4/nnm symmetry and parameters \(a = b = 3.799\,\text{Å},\) \(c = 6.093\,\text{Å},\) and \(V = 87.9\,\text{Å}^3\). The crystal lattice structure of pure FeTe\(_{0.65}Se_{0.35}\) is studied in Ref. 8 and is diagrammed in Fig. 1.
The saturation of FeTe\textsubscript{0.65}Se\textsubscript{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\textsuperscript{−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\textsubscript{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\textsuperscript{−3} mmHg for \(\sim 200\) 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
FeTe$_{0.65}$Se$_{0.35}$ crystals. Exposure to molecular hydrogen H$_2$ 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 H$_2$ 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 $T \geq 200$ °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°.

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 thermostatic dissociation of H$_2$ 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. 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 H$_2$ 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, $c = 6.0763$ Å, $V = 77.3$ Å$^3$ ($V/V_o = 13.76\%$), where $V$ is the initial volume of the unit cell of a crystal, and $V_o$ is the change in the volume of the cell. The orthohombic 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. 3), 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 $V = 77.2$ Å$^3$ ($V/V_o = 13.8\%$).

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 $V = 73.2$ Å$^3$ ($V/V_o = 14.6\%$) after a 5 h exposure to a hydrogen atmosphere at 5 atm. This temperature
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, H$_2$, and hydrogen atom impurities showed that they all contain a wide diffuse halo with a maximum near 2$\theta$ \approx 20° (Fig. 6), which shifts slightly to small diffraction angles 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...

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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 compositionally-similar Fe$_{1.01}$Te$_{0.56}$Se$_{0.44}$ do not change the symmetry of the lattice when heated to 270 °C. There is also no change in the lattice type upon heating in vacuum to 400 °C 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 stage (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 H$_2$ 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 $T \geq 200$ °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 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


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