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STRUCTURAL, MAGNETIC AND ELECTRONIC CORRELATIONS IN NONCONVENTIONAL SUPERCONDUCTORS $FeTe_{1-x}Se(S)_x$ AND $RbFe_2Se(S)_2$

134.01 PHYSICS AND TECHNOLOGY OF MATERIALS

Summary of the doctoral thesis in physical sciences

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PURPOSE AND OBJECTIVES OF RESEARCH

The actuality of the subject

Iron-based superconductor pnictides and chalcogenides play a special role for the physics and materials science of advanced electronic materials. The research of these materials is important both from the point of view of deepening the general knowledge about unconventional superconductivity, which manifests itself through cooperative effects and the coexistence of superconducting and antiferomagnetic states, as well as from the perspective of their application in different fields of modern electronics and electrotechnics. In the search for new superconducting (SC) compounds, with high critical temperatures and advanced critical parameters, iron-based superconductors have been intensively investigated over the last ten years. The discovery in 2008 of the first superconductor compound $La(O_{1-x}F_x)FeAs$, with a critical temperature of 26 K [1] initiated intense research in the field of complex materials. Shortly, several groups of superconducting materials were discovered in the iron-base SC family with various composition and structure. The optimization of the properties of the superconducting compounds by different dopings and substitutions has led to the significant increase of the critical temperature, which reaches the record values of 55 K for bulk samples [2] and 65-100 K [3,4] for monolayers. The compositional and structural complexity of the SC iron pnictites and chalcogenides creates a fertile ground for the interaction of magnetic and superconductive states.

Among the iron-based superconducting materials, the chalcogenide compounds FeSe and $FeTe_{1-x}Se(S)_x$ differ in simple crystalline structure consisting of planes of iron ions arranged along the *c* axis in the tetragonal structure. They are considered as model materials for analyzing the mechanisms of unconventional superconductivity as there are no interplanar atoms as in the SC arsenides, which allows to investigate the magnetic and superconducting correlations outside the effects of the mediating ions. It has recently been established that the intercalation of FeSe with Rb ions allows to increase the critical temperature from T_c = 9 K (for FeSe) to T_c = 33 K for $Rb_2Fe_4Se_5$ [5]. An unusual property of these materials is the coexistence of the superconducting state with the antiferromagnetic (AFM) state with the Néel temperature T_N, which exceeds 550 K, with the strong local magnetic moments of the iron ions of about 3 μ_B. Due to the fact that the superconducting state of the intercalated compounds in the Rb-Fe-Se system exists in a very

narrow concentration range, it was very difficult to search for the correlations between the structural, magnetic and electronic properties. Recently it has been established that anion substitution allows to continuously vary the critical temperature and to highlight the electronic, structural and magnetic correlations, as well as to identify the mechanisms that lead to the occurrence of the unconventional SC state.

The interest of fundamental and applied research is due to the potential of the iron-based superconductors for the design of new electronic and electrotechnical devices. Therefore, the research of the chalcogenide compounds $Fe_{1+y}Te_{1-x}Se_x$ and $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$, which are model materials for studying magnetic and superconducting phenomena, justifies the relevance and importance of this research.

Purpose of the research: To investigate the structural, magnetic and electronic properties of the materials $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A = Rb, K, Cs; X = S, Se) and $Rb_{1-x}Fe_{2-y}Se_{2-z}S$, for the analysis of the mechanisms of superconductivity, of magnetic exchange and electronic correlations, and deepening knowledge in this actual field of solid state physics and materials science.

The specific objectives of the research include:

-elaboration of processes of synthesis of polycrystals and growth of SC single crystals of $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A = Rb, K, Cs; X = S, Se) and $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ with variable concentration of anion substitution;

-investigation of the physical properties of $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A = Rb, K, Cs; X = S, Se) and $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ systems depending on composition and anion substitution, which includes the study of sample stoichiometry, structural and magnetic analysis, determination of SC parameters, analysis of mechanisms of conductivity and heat capacity;

-determining the percolation threshold of the SC state, evidencing the correlation effects and establishing the phase diagrams of these systems.

METHODOLOGY OF SCIENTIFIC RESEARCH

The following methodologies and methods were used to address the research objectives:

- for preparation of polycrystals – solid state synthesis;
- for single crystal growth – methodology of Bridgman and flux methods;
- for analysis of the composition of samples – wavelength dispersion (WDS) and energy dispersion (EDX) spectroscopies;
- for structural analysis – powder and single crystal X-ray diffraction;
- for the analysis of magnetic properties – SQUID magnetometry;
- for the analysis of thermodynamic properties – differential scanning calorimetry;
- for the analysis of electronic properties – resistivity and heat capacity.

The methods used have a complementary character and allow to obtain reliable information about the fundamental electronic state, structural, magnetic and superconducting transformations.

The novelty and the scientific originality of the results:

- The technological regimes of growth were developed and optimized and the perfect poly- and single crystalline samples of $Fe_{1+x}Te$, $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A = Rb, K, Cs; X = S, Se), and $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ compounds have been obtained.
- The complex study of the structural, magnetic, thermodynamic and electronic properties of the aforementioned materials in a wide temperature range 1,8 K $\leq T \leq$ 700 K, and magnetic fields up to 9 T was performed.
- The main structural parameters (lattice parameters, ion positions, distances and angles between ions), magnetic parameters (magnetic transition temperature, effective magnetic moment, Curie-Weiss temperature), and superconducting parameters (critical temperature, upper critical field, critical current, Sommerfeld coefficient, density of states at the Fermi level) have been determined through which the basic physical states of these materials were explained.
- X-ray diffraction studies of unidimensional compounds $AFeX_2$ (A = K, Rb, Cs; X = S, Se) have demonstrated the single phase structure and the absence of impurities. Wavelength dispersion and energy dispersion X-ray spectroscopies revealed the stoichiometric composition of the samples. Magnetic susceptibility studies have established the AFM ordering. The linear behavior of the magnetic susceptibility above the Néel temperature T_N without saturation suggests the metallic character of the $AFeX_2$ compounds and implies a strong intrachain Fe-Fe exchange interaction.
- Magnetic investigations of $FeTe_{1-x}Se_x$ single crystals with different substitutions x ($0 \leq x \leq 0,5$) revealed the antiferromagnetic ordering in compounds with composition $Fe_{1+y}Te$, $FeTe_{0,1}Se_{0,9}$, and $FeTe_{0,2}Se_{0,8}$. For $FeTe_{0,2}Se_{0,8}$ samples, the spin-glass-like state was detected. For the compound $FeTe_{0,3}Se_{0,7}$, the coexistence of the AFM state with the filamentary SC state was suggested. The specific heat measurements for the $FeTe_{0,5}Se_{0,5}$ samples revealed an extremely low value of the residual Sommerfeld coefficient, which indicates a high volume of the SC phase (up to 97 %) and demonstrates the high quality of the prepared samples.
- Magnetic hysteresis measurements revealed high values of critical current density for the superconducting samples $FeTe_{0,5}Se_{0,5}$, which are attributed to the intrinsic inhomogeneity due to the disorder in the cationic and anionic positions. The critical current value of $2,3\times10^5$ A/cm^2 obtained for $FeTe_{0,5}Se_{0,5}$ represents the record value and is important for energy applications.
- For the first time, for compounds $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ it has been shown that the percolation

threshold of the superconducting state is reached at the substitution $z = 1,2$. The SC state was found to coexist with the AFM state, which persists in all samples independent on the substitution. The anisotropic character of the AFM state was established. The Néel temperature was found to decrease from 515 K for $z = 0$ to 472 K for $z = 2$, indicating the reduction of the AFM interactions.

- For the entire region of substitutions in the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system, the crystal structure with iron vacancies was established. It has been found that the temperature of the structural transition into vacancy-ordered state changes non-monotoniously with substitution: it decreases from 538 K (for $z = 0$), to 523 K for $z = 1,3$, and increases again up to 563 K for $z = 2$.

- It has been shown that at temperatures below 140 K, $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ samples with $z \leq 1,2$ manifest metallic conductivity, and at high temperatures the metal-semiconductor transition takes place. It was found that the ground state of the compounds with $z > 1,2$, including the sample with $z = 2$, is also metallic.

- With the increase of the substitution in $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$, a considerable reduction of the magnitude of the anomaly in the heat capacity at the transition into the superconducting state was established, indicating the reduction of the density of states at the Fermi level. This fact explains the observed suppression of the superconductivity with substitution in this system.

Theoretical importance and applicative value

This work contributes to the development of the technology for growing single crystals of unconventional superconducting materials based on iron chalcogenides, with lamelar structure and high transition temperatures. The experimental results obtained in the current research constitute a base for the development of the theory of unconventional superconductivity and may present the basis for new theoretical approaches regarding the coexistence of the superconducting and antiferromagnetic states and the effect of phase separation. The technical characteristics of the studied materials are of particular importance for evaluating the potential of their use in various modern electronic and electrotechnical applications.

SUMMARY OF CHAPTERS

The **Introduction** compartment describes the actuality and importance of the topic addressed, the purpose and objectives of the thesis, the theoretical importance and the applicative value of the obtained results, the approval of the obtained results, as well as the summary of the thesis chapters.

The **first chapter** presents the literature review on ternary chalcogenide compounds of the general formula $AFeX_2$ (where A = K, Rb, Cs; X = S,Se) with unidimensional magnetic structure and on Fe-based superconducting compounds with high critical temperatures representing a group of materials with remarcable magnetic properties and two-dimensional structure. The considerable

increase in interest on ternary iron chalcogenides has been observed since 2008 when the first superconductor in the iron pnictites and chalcogenides family with a critical temperature of 26 K was discovered [1]. At present, the family of Fe-based superconductors has been extended to over 100 members that are classified in four main classes. Each of these classes has a number of common physical features, but also specific characteristics. It is expected that highlighting these similarities and differences will help to understand the mechanisms of unconventional superconductivity. The properties of the ternary chalcogenide materials of the general formula $A\mathrm{Fe}X_2$, $\mathrm{Fe}_{1+y}\mathrm{Te}_{1-x}\mathrm{Se}_x$, and $\mathrm{Rb}_{1-x}\mathrm{Fe}_{2-y}\mathrm{Se}_{2-z}\mathrm{S}_z$ which were known at the beginning of the given research, are described. The gaps in the current research area are indicated and the need to develop a more in-depth study is demonstrated in order to highlight the mechanisms of unconventional superconductivity in Fe-based superconucting chalcogenides.

The **second chapter** describes the methodology and research methods used. The technology for obtaining compounds from the $A\mathrm{Fe}X_2$, $\mathrm{Fe}_{1+y}\mathrm{Te}_{1-x}\mathrm{Se}_x$, and $\mathrm{Rb}_{1-x}\mathrm{Fe}_{2-y}\mathrm{Se}_{2-z}\mathrm{S}_z$ systems is described. The methods of analysis of the composition of the samples using the Cameca SX50 microprobe are described. The methods of investigation of the structural properties by X-ray diffraction are described. The working principle of the SQUID magnetometer (MPMS-5, Quantum Design) used to determine the magnetic properties is also described. The electrical conductivity and heat capacity studies using PPMS system (Quantum Design) as well as details on differential scanning calorimetry performed with the PerkinElmer DSC-8500 apparatus are described.

The **third chapter** describes the crystal growth, and results of the structural, magnetic and specific heat investigations of the unidimensional magnetic compounds $A\mathrm{Fe}X_2$ (A = Rb, Cs, K; X = S, Se). The stoichiometric composition of the obtained samples is demonstrated by the WDS and EDX studies. The magnetic susceptibility study for the compounds $\mathrm{RbFeSe_2}$, $\mathrm{KFeSe_2}$, and $\mathrm{RbFeS_2}$ is performed in the paramagnetic region and in the state with the three-dimensional antiferromagnetic order below the temperature T_N. The absence of impurity phases in these materials was confirmed by structural and compositional studies. The experimental data indicate minimal deviations of the sample composition from the initial stoichiometry. The WDS measurements for the $\mathrm{KFeS_2}$ sample determined the composition $\mathrm{K_{1,065(16)}Fe_{0,986(27)}S_{2,000(25)}}$. Regarding the compound $\mathrm{RbFeSe_2}$, for this the composition $\mathrm{Rb_{0,98}Fe_{0,98}Se_{2,00}}$ was obtained.

From the XRD measurements performed on $A\mathrm{Fe}X_2$ samples, the main structural parameters, namely the lattice constants and the interatomic distances, were determined. X-ray diffraction studies confirmed the monoclinic structure, space group *C2/c* (Figure 1) of $A\mathrm{Fe}X_2$ (A = K, Rb, X = S, Se). Regarding analogs with Cs, it was established that $\mathrm{CsFeS_2}$ crystallizes in the orthorhombic system with the *Immm* space group, while $\mathrm{CsFeSe_2}$ has the *C2/m* monoclinic structure.

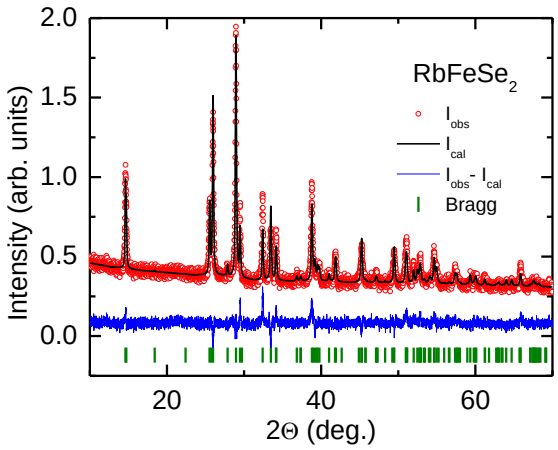

Fig. 1. X-ray powder diffraction profile of $RbFeSe_2$ crystal.

It has been established that the susceptibility of $RbFeSe_2$ single crystals manifests typical characteristics for unidimensional magnetic systems, with the transition into the AFM state at $T < T_N = 248$ K. Below T_N the susceptibility splits into two components: parallel and perpendicular with arrangement of the magnetic moments of spins along the crystallographic axis *b* ($H \perp c$). The magnetic susceptibility for $KFeS_2$ at $T < T_N = 252$ K has a behavior similar to $RbFeSe_2$. Above T_N, both compounds show a continuous linear increase of the susceptibility up to the highest temperatures of the measurements (720 K). This linear behavior is not characteristic for unidimensional Heisenberg chain antiferromagnetic compounds with localized spins, which usually exhibit a maximum in the susceptibility at temperature comparable with the intra-chain exchange. These data are in agreement with neutron diffraction and Mössbauer measurements [6].

Chapter four describes the preparation and investigation of $FeTe_{1-x}Se_x$ single crystals with different substitutions x ($0 \leq x \leq 0{,}5$; $x = 1$). It has been shown that the conditions for the preparation of the samples have a significant influence on their properties. The purity of the initial materials, as well as the mixing of the compounds in different environments are the main factors in obtaining the samples of high purity and quality.

The growth of $FeTe_{1-x}Se_x$ single crystals was carried out by the flux and Bridgman methods. In the growth methods, the melting temperature was varied between 700 °C and 1100 °C, and at the end it was maintained at 1100 ºC. The cooling speed was varied between 1 and 60 °C/h.

The analysis of the X-ray diffraction spectra for $Fe_{1+y}Te$ crystals and those calculated in the Rietveld program confirmed the tetragonal structure with *P4/nmm* symmetry and the lack of impurities. Figure 2 shows the X-ray diffraction profile for the $Fe_{1.057}Te$ sample. It has been confirmed that, in $Fe_{1+y}Te$, the Fe ions occupy two different positions: the tetrahedral position in

the plane for Fe1 and out of plane (interstitial) position for Fe2 ions. Among $Fe_{1+y}Te$ samples, the following compositions were studied: $Fe_{1,094}Te$, $Fe_{1,057}Te$, $Fe_{1,124}Te$, and $Fe_{1,15}Te$. The lattice constants for the $Fe_{1+y}Te$ compounds have the values: $a = b = 3,8259$ (2) Å and $c = 6,2832$ (6) Å.

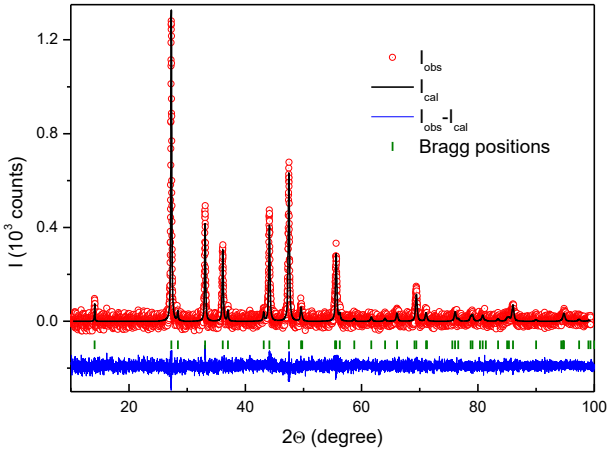

Fig. 2. X-ray powder diffraction profile of $Fe_{1,057}Te$ crystal.

Similar to the binary system FeTe, the crystal structure of the $Fe_{1+y}Te_{1-x}Se_x$ compounds ($0,1 \leq x \leq 0,5$), were indexed by the *P4/nmm* symmetry of the tetragonal structure. The influence of substitution on the lattice was established from the X-ray diffraction spectra that revealed a decrease of the parameters *a* and *c* as the concentration of selenium in the system increased.

From the magnetic susceptibility measured in the field of 10 kOe in the paramagnetic region, the main magnetic parameters of the $Fe_{1+y}Te$ materials (Curie-Weiss temperature θ_{CW} and the effective magnetic moment p_{eff}) were determined. It was found that below 400 K, the susceptibility increases continuously with the decrease of temperature down to the temperature T_N where it manifests a pronounced anomaly, after which the susceptibility drops sharply. Below the temperature of the phase transition into the antiferromagnetic state T_N the spin-density wave (SDW) ordering is established by the neutron diffraction studies [7]. For samples with excess of Fe, it was observed that the value of T_N decreases systematically from 65 K for the sample with $y = 0,057$ to 60 K for $y = 0,1$. The obtained negative values for θ_{CW} demonstrate the dominance of the AFM interactions in the $Fe_{1+y}Te$ compounds. The magnetic moments p_{eff} of the studied compositions are lower than the value of 4,9 μ_B expected for the localized Fe^{2+} ions in the high-spin state. It has been assumed that this difference between theoretical and experimental values reflect the fact that in these compounds there are existing magnetic ions with delocalized spins.

The magnetization curve for the $FeTe_{1-x}Se_x$ compounds with $0 \leq x \leq 0,3$ was found to be linear in character. From the analysis of the magnetic susceptibility it has been established that antiferromagnetic ordering is a particular feature for both the binary compounds $Fe_{1+y}Te$ and the

ternary compounds $FeTe_{0,9}Se_{0,1}$, $FeTe_{0,8}Se_{0,2}$, and $FeTe_{0,7}Se_{0,3}$ (Figure 3). The dependencies obtained for the $FeTe_{1-x}Se_x$ compounds (x = 0; 0,1; 0,2) show that with decreasing temperature to T_N the susceptibility increases. It has been established that, with the increase of substitution, the transition into the AFM state shifts to lower temperatures. At T_N for compounds with stoichiometry $FeTe_{0,9}Se_{0.1}$ and $FeTe_{0,8}Se_{0,2}$ the phase transition into the state with the AFM ordering takes place. For these compositions in the range of paramagnetic temperatures, the susceptibility follows a Curie-Weiss law which is assigned to the local moments. For the concentration of substitution x = 0,3, there is a continuous increase in the susceptibility on cooling without any anomaly at low temperatures. The susceptibility measurements for the $FeTe_{0,7}Se_{0,3}$ compound performed in weak field (10 Oe) applied parallel to the c axis, after cooling in the absence of the magnetic field (ZFC) show the transition into the superconducting state (Figure 4). The transition temperature for this composition is ~ 11 K. However, the susceptibility for this sample after field cooling cycle (FC) shows that the SC state is suppressed, which is typical for inhomogeneous superconductivity. Thus, for the $FeTe_{0,7}Se_{0,3}$, the filamentary superconductivity is suggested, with the SDW state probably coexisting with the SC state. For the $FeTe_{0,8}Se_{0,2}$ sample, the susceptibility in low fields show characteristics similar to the spin-glass-like state, the maximum susceptibility being found at the temperature T = 26,2 K (the inset in Figure 4). The inhomogeneities observed for this composition in the ZFC measurements at 10 K suggest the coexistence of the SDW state with the superconducting state.

Chapter five presents the macroscopic characterization of the single crystals of the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system with different substitutions (z = 0; 0,1; 0,25; 0,5; 1,0; 1,1; 1,2, 1,3, 1,4; 1,7, and 2,0). Growth, compositional analysis, structural data, magnetic properties (susceptibility, hysteresis, ZFC and FC susceptibilities), conductivity, differential scanning calorimetry, and thermal capacity are described here. The Bridgman method was used to grow single crystals. The mixture of the starting materials was carried out in the argon chamber with a residual oxygen and water content less than 1 ppm.

The initial materials were placed in double ampoules, pumped up to 10^{-3} mbar. The ampoules were heated to 1070 ^{o}C and kept for 5 hours at this temperature. Then, the ampoules were pulled down in the furnace with a gradient in the temperature of 300 ^{o}C with a rate of 3 mm/h. The concentration of the elements in the studied samples was determined on freshly cleaved samples using the Cameca SX50 analyzer. The WDS analysis did not detected any significant deviations in the S/Se ratio from the initial stoichiometry for all the samples studied. The concentration of Fe in the samples from different batches was found to be close to 1,6, which indicates the formation of compositions with Fe vacancies corresponding to the stoichiometry 245.

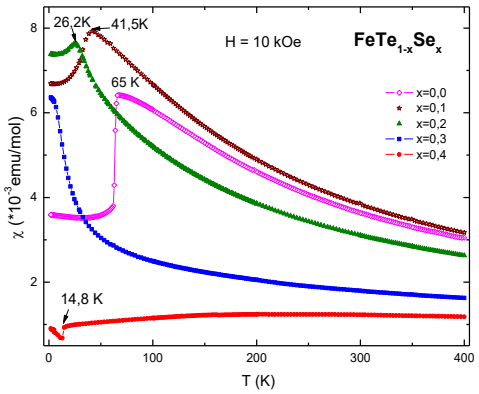

Fig. 3. Temperature dependence of magnetic susceptibility χ (T) for single crystalline $FeTe_{1-x}Se_x$ samples.

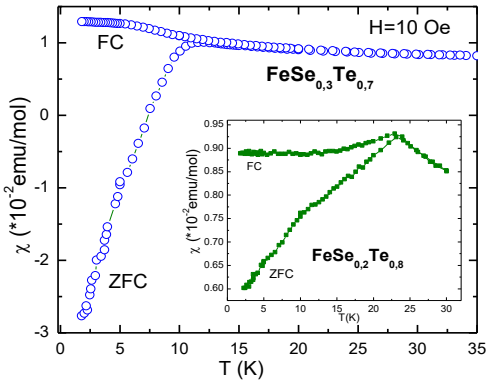

Fig. 4. Temperature dependence of the magnetic susceptibility for $FeTe_{0,7}Se_{0,3}$ sample measured after cooling in the field (FC) and in the absence of the field (ZFC).

For the samples without substitutions (z = 0), two different phases were observed with metallic stripes of micrometric sizes incorporated in the 245 phase. Under high resolution conditions, the composition of these stripes was determined, which corresponds to $Rb_{0,705(25)}Fe_{2,017(10)}Se_2$. Thus, it was established that the Fe content of the stripes corresponds to a phase 122 with Rb deficiency. It was found that even for the samples with the smallest substitution z = 0,1, it was not possible to detect the stripe structure in the micrometric range. At the same time, the presence of the AFM phase and coexisting metallic non-magnetic phase was detected in all samples by the Mössbauer experiments, indicating that phase separation in the crystals with anion substitutions is performed at a submicrometer level.

The X-ray structural analysis performed on single crystals from the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system revealed for all substitutions, the presence of the tetragonal cell with the lattice parameters $a(b)$ ~ 19 Å, and c ~ 14 Å. The initial crystal structure was resolved within the *I4/m* space group with the 5×5×1 supercell. The linear character of the variation of the parameters of the lattice parameters a and c with the substitution z has been established. Both parameters show a decrease with increasing sulfur content in accordance with the Vegard law, indicating the formation of the continuous solid solutions in the system. This fact, together with the absence of a further change in the lattice symmetry, suggests the statistical substitution of Se ions with S ions in the anion positions.

In addition to the initial structural model, structural refinement for all samples was also performed within √5×√5×1 cell, in the space group *I4/m*. To highlight the structural distortions and their evolution with substitution, the distances between the Fe ions, the distances between the Fe ions and the chalcogens Ch (Se or S), as well as the angles in the tetrahedra Fe2 and Fe1 were

analyzed. A monotonous decrease of Fe-Ch distances was found for both tetrahedral of Fe. The rate of decrease for all Fe-Ch distances was found to be much higher for substitutions *z* larger than 1,2. For substitutions in the range $z \leq 1,2$ the distances in the Fe2-Ch1 tetrahedron are larger than in the Fe1-Ch2 tetrahedron, but for $z > 1,2$ they become smaller. At the same time, for $z \leq 1,2$ the ratio of the three nearest equivalent distances Fe2-Ch2 to the distance Fe1-Ch2 changes only slightly, while for the substitutions $z > 1,2$ it begins to decrease essentially. The Fe1-Fe2 distance and the Fe2-Fe2 inter-cluster distance show a much stronger decrease with substitution than the Fe2-Fe2 intra-cluster distance. It is worth noting that the ratio of the Fe1-Fe2 distance to the Fe2-Fe2 inter-cluster distance, as well as the ratio of the Fe2-Fe2 intra-cluster distance to the Fe2-Fe2 inter-cluster distance, shows an opposite tendency with increasing substitution. We note at this point that the superconductivity in samples disappears at substitutions larger than $z = 1,2$. It is also worth mentioning that as the substitution increases, the ratio of intra-cluster and inter-cluster distances increases and approaches the unity, which suggests a more regular structural arrangement.

The investigation of the variation with the substitution of the angles for the tetrahedra Fe1 and Fe2 has established that in the tetrahedron Fe1 the four large angles α_1 and two small angles α_2 show a tendency of approaching the ideal angle 109 ° 47 with the increase of *z* up to 2,0. A similar trend is found for the four angles α_3, α_4, α_5 and α_6 in the Fe2 tetrahedron, while the other angles α_7 and α_8 of this tetrahedron decrease, and increase respectively with increasing substitution. The analysis of the regularity of the Fe tetrahedra, by comparing the sum of the angles at the vertices Ch1 and Ch2 shows that with the increase of the substitution from $z = 0$ to $z = 2$, the tetrahedron Fe2 becomes more regular indicating the decrease of the lattice distortions.

The differential scanning calorimetry (DSC) study for the sample without substitution ($z = 0$), revealed three pronounced anomalies that develop with increasing temperature from 300 K to 600 K (Figure 5 (a)). The neutron diffraction studies performed in [9] attributed the anomaly at the highest temperature T_s to a structural transition of the dominant phase 245 from the Fe-vacancy disordered state to a vacancy ordered state. The second anomaly at the temperature T_N was related to a transition of the dominant 245 phase into the AFM state. The anomaly at T_p, at the lowest temperature, was assigned to a phase separation temperature, where the 122 phase with Rb deficiency segregates from the 245 phase.

The analysis of the DSC data obtained for crystals of the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system showed that the anomalies recorded at T_s and T_p exhibit a pronounced hysteresis (up to 10 K) in the cooling and heating cycles indicating that they are related to the first-order structural transformations. The anomaly at T_N shows the lowest hysteresis (2-3 K) as expected for the second-order magnetic

transformation. It has been found that the intensities of the structural anomalies show significant variations that occur with increasing substitution. It has been established that the structural transitions show non-monotonic changes with the substitution, with a non-essential decrease of the values of T_s and T_p in the range $0 < z < 1,2$, followed by the significant increase of their values for $z > 1,3$. At the same time, the T_N changes monotonically from 518 K (for $z = 0$) to 470 K (for $z = 2$). The study of the susceptibility of the samples carried out at high temperatures (between 300 and 600 K) has confirmed the origin of the anomalies at T_N and T_p. A very good correlation of the temperature positions of the anomalies at T_s, T_p, and T_N was obtained in the DSC and the susceptibility data. Thus, it has become possible to compare the hysteresis behavior of these anomalies and to associate them with the structural and magnetic transformations.

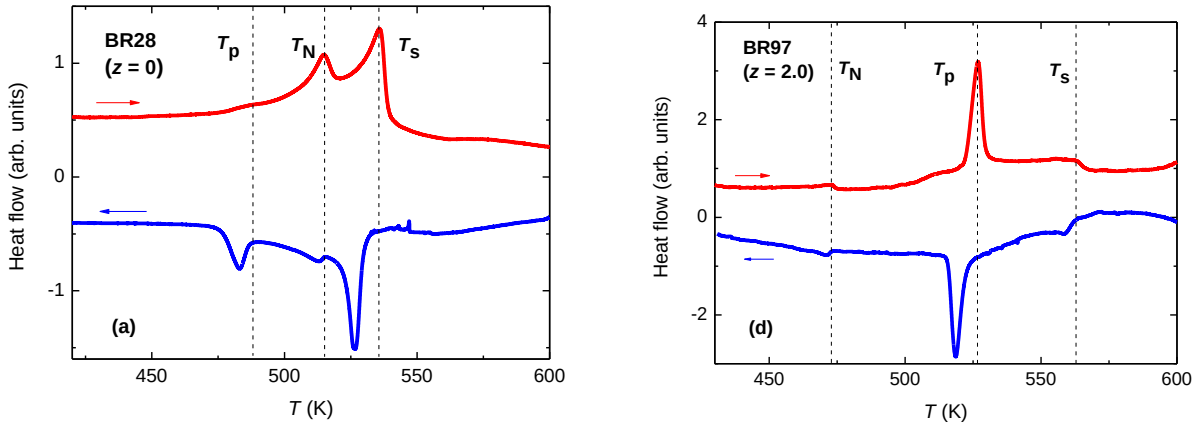

Fig. 5. Temperature dependencies of the DSC signal for crystals with substitution $z = 0$ (a) and $z = 2$ (b).

Magnetic measurements performed in the magnetic field of $H = 10$ kOe applied parallel to the c axis revealed that the susceptibility, $\chi_{\parallel}$ for the substituted samples, manifests a nonlinear increase with temperature (Figures 6 (a,b)). It has been found that for temperatures below 50 K, the susceptibility $\chi_{\perp}$ measured in the magnetic field applied perpendicular to the c axis has a much higher value and shows only a slight change in temperature. Such behavior of susceptibility $\chi_{\perp}$ and $\chi_{\parallel}$ has been established for all substitution samples and is a characteristic of an anisotropic antiferomagnet with the axis c being the direction of alignment of spins. Therefore, it was concluded that the anisotropic antiferromagnetism is a specific feature for the entire $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system.

The investigations of the temperature dependencies of the susceptibilities χ_{ZFC} and χ_{FC} for the superconducting samples with different substitutions measured in the field of $H = 10$ Oe applied parallel to the c axis have found a very low value of the FC susceptibility due to strong pining

effect (Figure 7). At the same time, the ZFC susceptibility value is significant and indicates a 100% shielding effect for samples with *z* up to 1,2. With an increase of the substitution from 0 to 1,2, a reduction of the transition temperature into the superconducting state from 32,4 K to 10 K was observed, with non-monotonous change for the substitution level of 1/4. The transition in the SC state for samples with up to 50% substitution (z = 1,0) is found to be very narrow.

The investigations of the temperature dependencies of the resistivity for the superconducting and non-superconducting samples have established their non-monotonous character, with semiconductor behavior at high temperatures, a maximum at the characteristic temperature T_m with the decrease of temperature followed by metallic behavior below the temperature T_m (Figures 8 (a, b). It was established that the temperature T_m shows a tendency towards smaller values with the increase of the substitution, except for the samples with z = 0,25 and 1,4. It was recorded that the residual resistivity for the superconducting samples with the substitution $z \leq 1{,}2$ shows a continuous increase with the increase sulfur content, which suggests a decrease of the density of states at the Fermi level and/or an increase of scattering of charge carriers due to disorder.

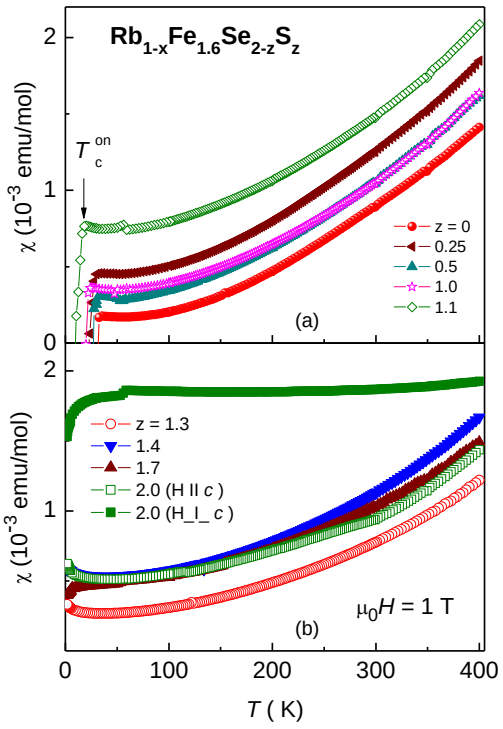

Fig. 6. Temperature dependencies of the susceptibility $\chi_{||}$ for superconducting (a) and $\chi_{||}$ and $\chi\perp$ for non-superconducting samples (b).

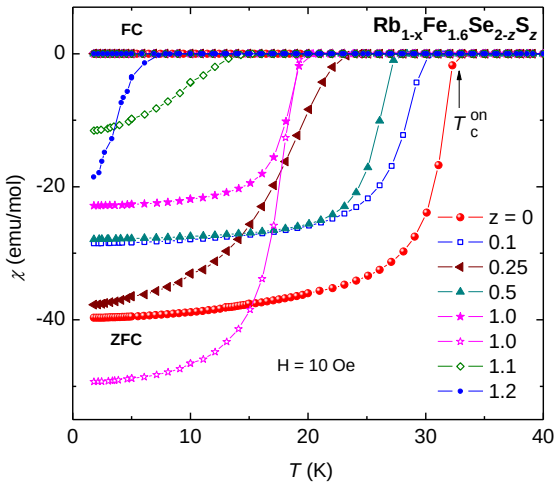

Fig. 7. Temperature dependencies of the ZFC and FC susceptibilities for different superconducting samples measured in the field of 10 Oe applied along the *c* axis.

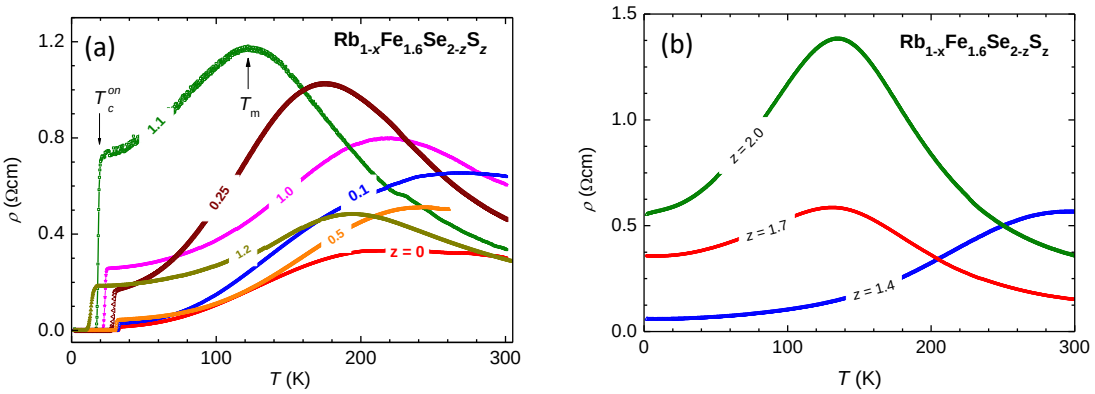

Figure 8. Temperature dependencies of the resistivity for the superconducting (a) and non-superconducting (b) samples from the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system.

The measurements of the resistivity in magnetic fields in the vicinity of the SC transition for samples with different substitution have found a shift to lower temperatures of the resistivity curves with the increase of the magnetic field (Figure 9). From these data, the upper critical fields $H_{c2}(T)$ were calculated using the criterion of 90% decrease of the resistivity in the normal state. The estimation of the upper critical field $H_{c2}(0)$ for T = 0 K was performed within the Werthamer-Helfands-Hohenberg model [9] using the relation $H_{c2}(0) = -0{,}69T_c(dH_{c2}(T)/dT)|_{Tc}$. It was established that the upper critical field $H_{c2}(0)$ increases from 22 T for the sample with z = 0 to 35 T for the sample with z = 0,25, but then decreases with the subsequent increase of the sulfur content, down to the value of 9 T for the sample with z = 1,1.

The studies of the specific heat C for the superconducting and non-superconducting samples carried out in the temperature range 1,8 - 300 K, has established their similar behavior which is dominated by the lattice contribution (Figure 10). For the SC samples, the anomaly at the critical temperature becomes visible only after subtraction of the lattice and magnetic contributions from the total specific heat (Figure 11).

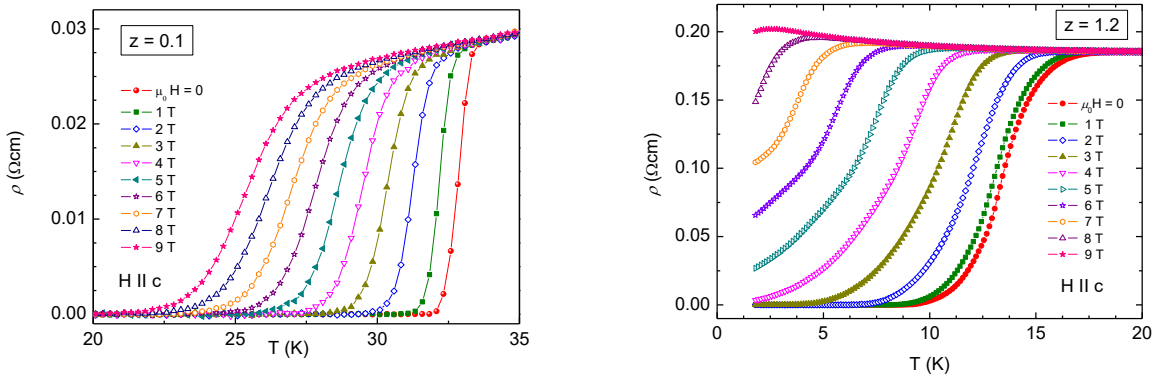

Fig. 9. Temperature dependencies of the resistivity in different magnetic fields near the SC transition for $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ with z = 0,1 and 1,2.

For modeling the phonon and magnetic contributions to C, the data for the specific heat for the non-superconducting sample $Rb_{0,75}Fe_{1,5}Se_2$, which exhibits magnetic properties similar to the properties of the SC sample $Rb_{0,8}Fe_{1,6}Se_2$ with $C_{lat}(0)$ for $z = 0$ [5], and $Rb_{0,8}Fe_{1,6}S_2$ with $C_{lat}(2)$ for $z = 2$ were used. The linear character of the C/T dependence on T^2 at temperatures below 10 K was established for samples with $z = 0$; 1; and 2 (the inset of Figure 10). Therefore, the experimental data at temperatures below 4 K were fitted by the expression $C/T = \gamma + \beta T^2$, where γ represents the coefficient for the linear term and the factor β characterizes the contributions of the lattice and magnons to the specific heat, both being proportional to T^3 and cannot be estimated independently. The temperature θ_D was calculated using the relation $\theta_D = [12\pi^4 k_B N_A Z/(5\beta)]^{1/3}$, where k_B and N_A are the Boltzmann and Avogadro constants, and Z = 5, is the number of atoms in the elementary cell. It was established that the values for parameter γ vary between 0,08 and 0,3 mJ/(mol×K^2) for samples with the substitution $z \leq 1{,}1$, which suggests an insignificant amount of impurities. For samples with $z \geq 1{,}2$, the value of parameter γ was found to increase significantly, which indicates an increase of the amount of the metallic phase. The value of the β-factor shows a continuous decrease as the substitution increases. The value of the Sommerfeld coefficient in the normal state γ_n for the SC samples was calculated from the temperature dependence of the electronic specific heat using the entropy conservation at the temperature T_c, according to the expression:

$$\int_0^{T_c} \frac{C_{el}}{T} dT = \int_0^{T_c} \gamma_n dT$$

The analysis of the specific heat data in zero field, revealed a wing at temperatures above T_c indicating SC fluctuations and a second wing at temperatures between 20 and 27 K, which suggests the presence of an additional density states which can be associated with the SC state without percolation due to intrinsic inhomogeneities of the samples. It was established that for the sample with $z = 0$ with the lowest obtained value $\gamma_n = 6{,}2$ mJ/(mol×K^2), the reduced specific heat jump at T_c, $\Delta C/\gamma_n T_c$, has a value 1,31, which is less than 1,43 for the BCS theory for weak coupling. It has been established that the magnitude of the anomaly λ at T_c shows a continuous decrease with substitution (Figure 11) which suggests a reduction of the volume of the superconducting phase. It has been established a reduction in the value of C_{el} and the Sommerfeld coefficient γ_n that takes place with the increase of substitution. It was concluded that the observed suppression of the superconductivity with increasing substitution is accompanied by the reduction of the density of states at the Fermi level.

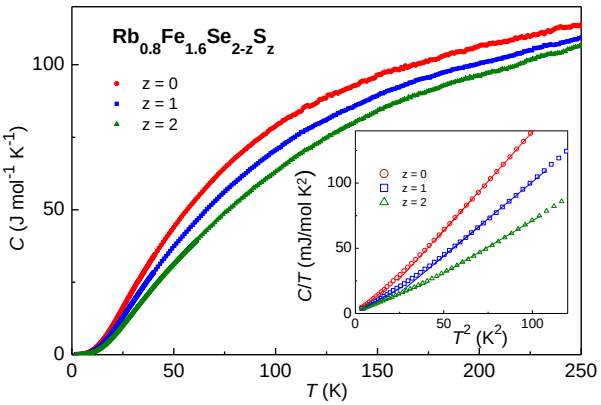

Fig. 10. Temperature dependencies of the specific heat *C* for samples with different substitutions in the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system.

This conclusion was confirmed by the experimental data of the difference in the specific heat *C* measured in the zero field and in the field of 9 T. It was found that with the increase of the substitution *z* from 0 to 1 there is a significant reduction, almost 6 times, of the magnitude of the anomaly λ at T_c. A reduction from 3 to 4 times was obtained for the parameter γ_n for these samples. It was noticed that the reduction of the density of Fermi states with the substitution derived from the specific heat data is in good agreement with the results of the paper [10]. There it was shown that with the increase of the substitution of S for Se, the orbital-selective Mott transition shifts to higher temperatures due to reduction of the correlations in the d_{xy} channel. Therefore, the observed reduction of the superconducting temperature T_c in the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system was attributed to this mechanism.

The summary of the results of the studies performed on the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ samples, allowed us to construct for the first time the phase diagram of this system (Figure 12). It has been established that at the lowest temperatures, the ground state of the samples with the substitution $z \leq 1,2$ is superconducting. As the substitution increases, a reduction of the transition temperature into the SC state occurs. The percolation threshold of the SC state is located between concentrations 1,2 and 1,3. The SC state coexists with the AFM state that is revealed in all samples independent on the substitution. The transition temperature into the AFM state shows a monotonous decrease, which indicates a reduction of the AFM interactions with increasing substitution. While AFM correlations are important for the SC state, the reduction of the AFM interactions may contribute to suppression of the superconductivity observed in this system. This fact reminds on the influence of pressure on samples $Rb_{0,8}Fe_{1,6}Se_2$, which revealed that the suppression of the SC phase occurs simultaneously with the suppression of the AFM phase [11]. The AFM phase has an ordered

structure of Fe vacancies below the structural transition at T_s. The temperature of the structural transition T_s. shows an insignificant decrease with increasing substitution up to z = 1,3 and then increasing again for larger substitutions.

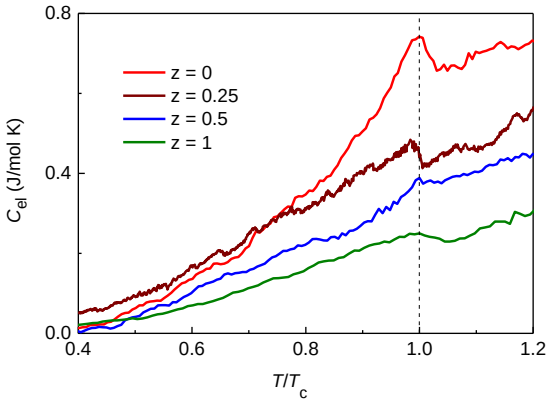

Fig. 11. The temperature dependencies of the electronic specific heat C_{el} for the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ samples with different substitutions.

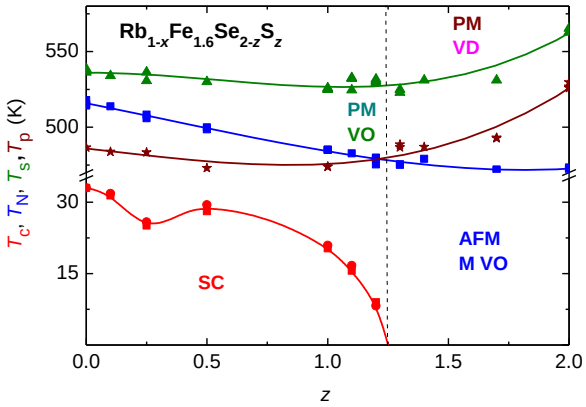

Fig. 12. *T*-*z* phase diagram for the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system.

GENERAL CONCLUSIONS

Following the research carried out in the thesis, the following conclusions were formulated:

- The technological regimes of growth have been developed and optimized and perfect poly- and single crystalline samples of iron chalcogenides have been obtained, namely, $Fe_{1+x}Te$, $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A = Rb, K, Cs; X = S, Se), and $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$;

- The complex study of the structural, magnetic, thermodynamic and electronic properties of the compounds $Fe_{1+x}Te$, $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A = Rb, K, Cs; X = S, Se), and $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ was performed over a wide temperature range 1,8 K ≤ T ≤ 700 K, and magnetic fields up to 9 T;

- The single phase composition and the absence of impurities in the single crystals of unidimensional compounds $AFeX_2$ (A = K, Rb, Cs; X = S, Se) were demonstrated. Wavelength dispersion X-ray spectroscopy revealed the stoichiometric composition of the obtained samples. It was found that the magnetic susceptibility is typical for the unidimensional materials in the paramagnetic region and shows the antiferromagnetic ordering. The linear behavior of the magnetic susceptibility above the temperature T_N without saturation assumes the metallic character of the $AFeX_2$ compounds and implies a strong intra-chain Fe-Fe exchange interaction.

- The main structural parameters of $FeTe_{1-x}Se_x$ single crystals with different substitutions (0

$\leq x \leq 0{,}5$) were determined by X-ray diffraction studies and Reitveld analysis. Magnetic studies have revealed the antiferromagnetic ordering in the compounds $Fe_{1+y}Te$, $FeTe_{0,1}Se_{0,9}$, and $FeTe_{0,2}Se_{0,8}$. For $FeTe_{0,2}Se_{0,8}$ samples, the spin-glass-like state was detected. For $FeTe_{0,3}Se_{0,7}$ sample, the magnetic measurements demonstrated the possible coexistence of the antiferromagnetic state with the filamentary superconducting state.

- Magnetic hysteresis measurements revealed high values of the critical current density for the superconducting samples $FeTe_{0,5}Se_{0,5}$, which are attributed to the intrinsic inhomogeneities due to disorder in the cationic and anionic positions. The value of $2{,}3\times10^5$ A/cm^2 for the critical current is the highest value reported for the $FeSe_{1-x}Te_x$ system and indicates the high current carrying capacity in these materials, which is of significant importance for energy applications.

- For the first time, for the compounds $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ it was shown that the percolation threshold of the superconducting state is reached at the concentration of the substitution $z = 1{,}2$. It was shown that the superconducting state coexists with the antiferromagnetic state that persists in all samples regardless of the substitution. The anisotropic character of the antiferromagnetic state was established. The Néel temperature was found to decrease with substitution from 515 K for $z = 0$ to 472 K for $z = 2$, indicating reducing of the antiferromagnetic interactions.

- For the entire region of substitutions in the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system, the crystal structure with iron vacancies was established. It has been found that the temperature of the structural transition in the state with the ordered vacations changes non-monotonously with the substitution.

- It has been shown that at temperatures below 140 K, $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ samples with substitutions $z \leq 1{,}2$ show metallic conductivity, and at high temperatures the metal-semiconductor transition takes place. It was found that the ground state of the compounds with concentration larger than 1,2, including the sample with $z = 2$, is also metallic.

- A considerable reduction of the anomaly in the heat capacity at the transition into the superconducting state was found on increasing substitution in the $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system, which indicates the reduction of the density of states at the Fermi level. This explains the suppression of the superconductivity observed with increasing substitution in this system.

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SUMMARY

Identification data: The thesis „*Structural, magnetic and electronics correlations in nonconventional superconductors* $FeTe_{1-x}Se(S)_x$ *and* $RbFe_2Se(S)_2$ **”** is prezented by Mrs. Dorina Croitori for the Ph.D degree in Physical Sciences. The dissertation has been completed in Chisinau in 2019. The field of research „Materials sciences and technology”.

Structure of thesis: introduction, five chapters, general conclusions and recomendations, bibliografy by 154 tittles, 86 pages of text, 87 of figures, 18 tables. The obtained results are published in 18 papers and abstracts.

Keywords: nonconventional superconductors, antiferromagnetism, phase separation.

Scope of work: preparation and investigation of structural, magnetic, and thermodinamic properties of iron chalcogenides $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A = Rb, K, Cs; X = S,Se), and $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ with uni- and bidimensional structure. Analisis of the mecanisms of superconductivity, magnetic exchange, of structural and electronic correlations.

Research objectives: development of the technology of synthesis of polycrystals and growth of single crystals of $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A = Rb, K, Cs; X = S,Se) and $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ with variable composition and concentraton of anion substitution. Investigation of physical properties of compounds in function of their composition and substitution in a large range of temperature (1.8 K-700 K) and magnetic fields (up to 9 T). Study of sample stoichiometriy, structural and magnetic analysis, determination of superconductor parameters, analysis of mecanisms of conductivity and of thermodynamic properties having the main scope to evidentiate the structural, magnetic, and electronic correlations.

Novelty and scientific originality: The perfect single crystals of $Fe_{1+x}Te$, $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A = Rb, K, Cs; X = S, Se), and $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ with record values of superconducting and magnetic properties have beed grown. The principal structural, magnetic, and superconducting parameters and their variation with substitution have been determined. The percolation treshold for the superconducting state in $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system have been established. The anisotropic character of the antiferromagnetic order which coexists with the superconducting state within the phase separated scenario was evidenced. The vacancy ordering of Fe ions and the character of the structural transitions into desordered and phase separated state was revealed. It was demonstrated that the suppression of superconducting state is caused by the reduction of the density of states at the Fermi level. For the first time, the phase diagram of $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ system which describes physical ground states, structural, magnetic, and electronic correlations was established.

Obtained resuls that contribute to solution of important scientific problem: The technology of the growth of perfect single crystals $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A = Rb, K, Cs; X = S, Se), and $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ with variable composition and concentration of anion substitution with performant magnetic and superconducting parameters of prospective for application in advanced electronics and electrotechics was developed. The mechanisms that govern the change of the physical properties of materials under study in function of composition and substitution concentration were established.

Theoretic value: The experimental results obtained for the first time in the thesis constitue the fundamental base for development of theory of nonconventional superconductivity and can form the base for new theoretical approaches related to phenomenon of coexistence of superconducting and antiferromagnetic states and to effect of phase separation.

Applied value: Advanced technical characteristics of the studied materials and their applied potential are of particular importance for design of novel electronics and electrotechnic devices.

Implementation of scientific results: The obtained results were presented at a number international and national științific conferences and published in national and international journals with IF.

АННОТАЦИЯ

Идентификационные данные: Диссертация „*Структурные, магнитные и электронные корелляции в нетрадиционных сверхпроводниках* $FeTe_{1-x}Se(S)_x$ *и* $RbFe_2Se(S)_2$ **”** представлена Дориной Кроиторь на соискание ученой степени доктора в физике. Работа выполнена в Кишиневе в 2019 г. Научное направление „Материаловедение и технология материалов.

Струкутура диссертации: введение, пять глав, основные выводы и рекомендации, библиография содержит 154 ссылки, 86 страниц основного текста, 87 рисунков, 18 таблиц. Полученные результаты опубликованы в 18 статьях и тезисах докладов.

Ключевые слова: нетрадиционные сверхпроводники, антиферромагнетизм, фазовая сепарация.

Цель работы: получение и исследование структурных, магнитных и термодинамических свойств халькогенидов железа $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A = Rb,K,Cs; X=S,Se), и $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ с одномерной и двумерной структурой. Анализ механизмов сверхпроводимости, магнитного обмена, структурных, магнитных и электронных корелляций в данных материалах.

Задачи исследований: разработка технологии синтеза поликристаллов и выращивания монокристаллов $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A=Rb,K,Cs; X=S,Se), и $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ с вариацией состава и концентрации анионного замещения. Исследование физических свойств образцов в зависимости от состава и замещения в широком диапазоне температур (1.8 K-700 K) и магнитных полей (до 9 T). Исследование стехиометрии, структурный и магнитный анализ, определение сверхпроводящих параметров, анализ механизмов проводимости и термодинамических свойств с целью выявления структурных, магнитных и электронных корелляций в данных материалах.

Научная новизна и оригинальность: Были получены совершенные монокристаллы $Fe_{1+x}Te$, $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A=Rb,K,Cs; X=S,Se), и $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ с высокими значениями сверхпроводящих и магнитных параметров. Были определены основные структурные, магнитные и сверхпроводящие параметры и их вариация в зависимости от замещения. Был определен порог перколяции сверхпроводящей фазы в системе $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$. Был выявлен анизотропный характер антиферромагнитного упорядочения, сосуществующего со сверхпроводящим состоянием в виде сепарированных фаз. Установлено упорядочение вакансий ионов железа и выявлен характер структурных переходов в разупорядоченное состояние и фазовой сепарации. Показано, что подавление сверхпроводимости вызвано уменьшением плотности состояний на уровне Ферми. Впервые построена полная фазовая диаграма системы $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$, которая описывает основные физические состояния, структурные, магнитные и электронные корелляции в данных материалах в зависимости от замещения.

Результаты, которые вносят вклад в решение важной научной проблемы: Была разработана технология и выращены совершенные монокристаллы $Fe_{1+y}Te_{1-x}Se_x$, $AFeX_2$ (A=Rb,K,Cs; X=S,Se), и $Rb_{1-x}Fe_{2-y}Se_{2-z}S_z$ с вариацией состава и концентрации анионного замещения, с высокими значениями сверхпроводящих и магнитных параметров, перспективные для применения в современной электронике и электротехнике. Были установлены механизмы, которые приводят к изменению физических свойств материалов в зависимости от состава и концентрации замещения.

Теоретическое значение: Полученные впервые в работе экспериментальные результаты важны для развития фундаментальной базы, в частности, для развития теории нетрадиционных сверхпроводников, и могут определить новые теоретические подходы, касающиеся сосуществования сверпроводящих и антиферромагнитных состояний и эффекта фазовой сепарации.

Практическая значимость: Высокие значения технических характеристик исследованных материалов имеют важное значение и высокий потенциал для использования в различных областях современной электроники и электротехники.

STRUCTURAL, MAGNETIC AND ELECTRONIC CORRELATIONS IN NON-CONVENTIONAL SUPERCONDUCTORS $FeTe_{1-x}Se(S)_x$ ȘI $RbFe_2Se(S)_2$

134.01 PHYSICS AND TECHNOLOGY OF MATERIALS

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