Concentration dependences of the structural, magnetic and kinetic properties of manganese chalcogenides doped with tellurium

O B Romanova\textsuperscript{1,2}, M N Sitnikov\textsuperscript{1}, Yu Yu Loginov\textsuperscript{1} and Abdelbaki Hichem\textsuperscript{1}

\textsuperscript{1}Reshetnev Siberian State University of Science and Technology, 31 Krasnoyarskii rabochii prospekt, Krasnoyarsk, 660037, Russia
\textsuperscript{2}Kirensky Institute of Physics SB RAS, 50/38 Akademgorodok St., Krasnoyarsk, 660036, Russia

E-mail: rob@iph.krasn.ru

Abstract. The effect of anionic substitution on the structural, magnetic, and kinetic properties of chalcogenides of the MnSe\textsubscript{1-X}Te\textsubscript{X} system in the temperature range of 77-400K in magnetic fields up to 12 kOe was studied. With an increase in the substitution concentration, changes in the structural and magnetic characteristics, which correlate with changes in the electronic structure, were found. The type and mobility of the main current carriers were determined from the Hall effect measurements.

1. Introduction

Magnetic semiconductors undergoing electronic [1–4] and magnetic phase transformations [5–8], both in temperature and in concentration, are promising materials for the development and creation of an element base of microelectronics. The interaction of the magnetic and elastic subsystems leads to a change in the magnetic structure, to new magnetic phases in which the electronic structure and kinetic properties can change [9-11]. Such substances include MnSe\textsubscript{1-X}Te\textsubscript{X} solid solutions synthesized on the basis of manganese monoselenide. These compounds show a polaron conduction mechanism, which is sensitive to the slightest changes in the electronic structure, as well as in the unit cells of the magnetic and crystalline subsystems.

Manganese chalcogenides MnSe and MnTe reveal structural, magnetic transitions and a change in transport properties from semiconductor to metallic at temperatures below 300 K. The initial compound manganese monoselenide (MnSe) is an antiferromagnet with $T_N$=135K [12-14]. In the temperature range 248 K <T <266 K, MnSe exhibits a structural phase transition from the cubic phase of the NaCl type to NiAs, and below this temperature, these two phases coexist in the sample [15]. MnTe crystallizes in the hexagonal type of NiAs structure and is an antiferromagnetic with a Neel temperature of 310 K. MnSe and MnTe are p-type semiconductors with an energy gap in the spectrum of single-particle electronic excitations for MnSe equal to (2.0-2.5 eV), and for MnTe (0.9-1.3 eV), respectively [16, 17]. In MnSe the magnetoresistance effect was detected in the range Néel temperature, while there is no effect in manganese monotelluride and it is observed only in thin-film samples [18, 19].

The aim of this work is to study the effect of anionic substitution on the structural, magnetic and kinetic properties of chalcogenides MnSe\textsubscript{1-X}Te\textsubscript{X} (0≤X≤0.4) solid solutions.
2. Results and Discussion

Anion-substituted \( \text{MnSe}_{1-x}\text{Te}_x \) solid solutions with a substitution concentration \( 0 < X < 0.4 \) were synthesized by the solid-phase reaction method using a stepwise mode. The synthesis technique is described in detail in [12].

X-ray diffraction pattern of the powders of the studied compositions were obtained at \( T = 300 \text{ K} \) on DRON-3 X-ray diffractometer (Cu\( K_a \) radiation). X-ray data show that anionic substitution in the \( \text{MnSe}_{1-x}\text{Te}_x \) system with an increase in tellurium content leads to a noticeable decrease of the intensity of reflexes. The decrease in the intensity of diffraction reflections in X-ray diffraction pattern is due to the fact that the formation of solid solutions at substitution in the anion sublattice, is accompanied by significant crystalline distortions and increase in the unit cell parameter \( a \) (table 1). The growth of a disorder in the whole cubic structure with a spatial group \( Fm3m \) (225) is observed. An increase in the cell parameter with growing tellurium concentration allows us to draw a conclusion about the formation of solid solutions of the \( \text{MnSe}_{1-x}\text{Te}_x \) system.

In order to establish the effect of anion substitution on the magnetic subsystem and the possibility of the formation of magnetically inhomogeneous states in the initial MnSe matrix, the magnetic properties of the synthesized samples of the \( \text{MnSe}_{1-x}\text{Te}_x \) system \((0 < X < 0.4)\) were studied using the Faraday method in a magnetic field of \( 8.6 \text{ kOe} \) in the temperature range 80-1000K on samples placed in evacuated quartz ampoules. Table 1 presents the basic magnetic characteristics of the synthesized samples of the \( \text{MnSe}_{1-x}\text{Te}_x \) system. With an increase in the substitution concentration, there is a significant decrease in the temperature of the magnetic phase transition \( (T_N) \) and paramagnetic Curie temperature \( (\Theta_c) \) in absolute value, which indicates an increase in ferromagnetic exchange. This assumption confirms the hysteresis of the magnetic susceptibility found in the temperature range 80-350 K for all samples, but it is most pronounced for the composition \( X = 0.2 \). With increasing concentration, the magnetic moment decreases from 5,50 \( \mu_B \) for \( X = 0.1 \) to \( \sim 5,13 \mu_B \) for \( X = 0.4 \). Substitution of selenium by tellurium leads to an anomalous behavior of the susceptibility in the vicinity temperature of the magnetic phase transition \( \sim 330 \text{K} \) for pure MnTe. This behavior of the susceptibility is probably due to the formation of inhomogeneous states (nanoclusters) of the MnTe compound in the matrix of the \( \text{MnSe}_{1-x}\text{Te}_x \) solid solution.

Table 1. Magnetic characteristics of the \( \text{MnSe}_{1-x}\text{Te}_x \) system.

| Состав, X | 0.1 | 0.2 | 0.3 | 0.4 |
|----------|-----|-----|-----|-----|
| \( a \), nm | 0.548 | 0.554 | 0.558 | 0.562 |
| \( T_N \), K | 135 | 130 | 125 | 120 |
| \( Q_p \), K | -350 | -330 | -300 | -275 |

Changes in the structural and magnetic characteristics correlate with changes in the electronic structure with increasing substitution concentration. A similar correlation of changes in the electronic and crystalline structures was observed in bismuth pyroskites [20, 21]. The electrical resistivity was measured by the standard four-probe direct current method in the temperature range 77-300 K in a magnetic field of up to 12 kOe and indicates the semiconductor type of conductivity of the synthesized compounds of the \( \text{MnSe}_{1-x}\text{Te}_x \) system. A change in the substitution concentration leads to a decrease in the electrical resistivity (figure 1a), which correlates with the data of magnetic properties. In this case, the activation energy \( \Delta E \approx (0.07-0.09) \text{ eV} \) is practically independent of the composition of this system samples.

The influence of the magnetic field on the transport characteristics with a change in concentration was determined from the current-voltage characteristics measured in a zero magnetic field and in a field of \( H = 10 \text{ kOe} \). The experiment showed that the obtained dependences \( U \) \( (I) \) are linear and do not depend on the magnitude of the applied magnetic field at temperatures below 100K. It was established that in the magnetic field the resistance of the samples decreases and the greatest change is found in the vicinity of the Néel temperature for \( X = 0.1 \), it is 100% (figure 1b). With an increase in the substitution concentration, the magnitude of the magnetoresistance \( (\delta_H) \) decreases in absolute value and \( \delta_H \sim 5\% \) for the composition \( X = 0.2 \) is observed in the paramagnetic area. This value is much
smaller in comparison with magnetoresistance in solid solutions based on manganese sulfide [22-24].
A further increase in concentrations to \( X = 0.4 \) leads to the disappearance of the effect. One possible explanation for the decrease in resistance in a magnetic field for composition \( X = 0.1 \) is an increase in the electron localization radius in potential wells as a result of competition between ferromagnetic and antiferromagnetic interactions and a reduction in the width of the potential barrier.

![Figure 1](image1.png)

**Figure 1.** Concentration dependences of the conductivity (a) and the relative magnitude of the magnetoresistance (b) at \( T = 130K \) for the MnSe\(_{1-x}\)Te\(_x\) system.

To determine the sign and mobility (\( \mu \)) of the current carriers, the Hall effect was measured. The galvanomagnetic properties of anion-substituted MnSe\(_{1-x}\)Te\(_x\) solid solutions were studied in magnetic fields up to 12 kOe in the temperature range 77–400K.

![Figure 2](image2.png)

**Figure 2.** Temperature dependences of the Hall constant for concentrations \( X = 0.1 \) (a) and 0.3 (b). The inset shows the temperature dependence of mobility for these concentrations.

The manganese monoselenide MnSe has a p-type conductivity. For small substitution concentrations \( X = 0.1 \), with increasing temperature (figure 2a), the Hall coefficient (R\(_H\)) increases and at a temperature of 140K the sign of the Hall constant changes in the field where the maximum magnetoresistive effect is observed [25]. In the temperature range 140-347K, the hole type of
conductivity dominates with a sharp decrease in the $R_H$ at $T = 320K$. An increase in the anion substitution of selenium with tellurium in the MnSe$_{1-X}$Te$_X$ system leads to a change in the sign of current carriers. For the concentration $X = 0.3$, the dependence $R_H(T)$ shows negative values, which indicates the electronic type of the carrier type (n-type) in the entire temperature range of measurements in fields up to $H \sim 12$ kOe. In the temperature range $190-250K$, the $R_H(T)$ dependence has an anomaly, which is due to the presence of charge carriers of different signs in the solid solutions of the MnSe$_{1-X}$Te$_X$ system, given that the initial compound is p-type semiconductors, as well as an increase or decrease in their number at different temperatures and with the mobility of charge carriers. The presence of an anomaly on $R_H(T)$ correlates with the magnetization hysteresis observed in this temperature range. It should be noted that in MnSe a sharp maximum of magnetic susceptibility is observed in the temperature range $T = 160K - 180K$, exceeding the Neél temperature in the cubic modification. In the same temperature range, upon cooling and heating of the MnSe single crystal in the temperature behavior of the resistance, hysteresis is observed, which corresponds to the coexistence of cubic and hexagonal modifications [16, 26]. Moreover, for MnSe, the resistance hysteresis has the form of a loop (as infinity), which depends on the rate of change of the measurement temperature. The mobility of the main current carriers is determined from the Hall effect measurements. It was found that the MnSe$_{1-X}$Te$_X$ system is characterized by small mobility values, which decrease with increasing $X$.

3. Conclusion
It has been found that anionic substitution of selenium by tellurium leads to an increase in the unit cell parameter of the fcc lattice of the NaCl type of antiferromagnetic samples of the MnSe$_{1-X}$Te$_X$ system in the space group $Fm\bar{3}m$ (225). It was determined that an increase in the concentration ($X$) of substitution leads to a decrease in the Neél temperature and magnetic moment within 20% and the magnitude of the magnetoresistive effect. The value of the energy activation, which changes slightly with increasing concentration, was defined. A correlation between the behavior of the magnetization of the samples and the temperature dependence of the magnetoresistance and galvanomagnetic properties was found. Using the Hall effect measurements, for $X=0.1$ a change carrier types by temperature has been found. With increasing concentration to $X = 0.3$, electrons become dominant.

Acknowledgments
The reported study was funded by RFBR according to the research project №20-52-00005 Bel_a.

References
[1] Petrakovskii G A, Loseva G V, Ryabinkina L I and Aplesnin S S 1995 JMMM 140-144 147
[2] Aplesnin S S, Ryabinkina L I, Romanova O B, Sokolov V V, Pichugin A Y, Galyas A I., Demidenko O F, Makovetski G I and Yanushkevich K I 2009 Phys. Sol. St. 51 698
[3] Aplesnin S S, Romanova O B, Harkov A M, Balaev D A, Gorev M V, Vorotinov A M, Sokolov V V and Pichugin A Yu 2012 Phys. St. Sol. (B) 249 812
[4] Pal S, Banerjee A, Rozenberg E and Chaudhuri B K 2011 J. Appl. Phys. 89 4955
[5] Aplesnin S S, Ryabinkina L I, Romanova O B, Velikanov D A, Balaev A D, Balaev D A, Yanushkevich K I, Galyas A I, Demidenko O F and Bandurina O N 2008 J. Exp. Theor. Phys. 106 765
[6] Petrakovskii G A, Ryabinkina L I, Velikanov D A, Aplesnin S S, Abramova G M, Kiselev N I and Bobina A F 1999 Phys. Sol. St. 41 1520
[7] Aplesnin S S, Romanova O B, Gorev M V, Velikanov D A, Gamzatov A G and Aliev A M 2013 J. Phys. Cond. Matt. 25 025802
[8] Efrem D'Sa J B C, Bhobe P A, Priolkar K R, Das A, Krishna P S R, Sarode P R and Prabhu R B 2004 Pramana J. Phys. 63 227
[9] Aplesnin S S 1998 J. Phys. Cond. Mat. 10 10061
[10] Aplesnin S S 2000 Phys. Rev. B 61 6780
[11] Aplesnin S S, Romanova O B, Korolev V V, Sitnikov M N and Yanushkevich K I 2017 *J. Appl. Phys.* **121** 7
[12] Aplesnin S S, Romanova O B, Gorev M V, Vasil'ev A D, Demidenko O F, Makovetskii G I and Yanushkevich K I 2012 *Phys. Sol. St.* **54** 1374
[13] Decker D I and Wild R L 1971 *Phys. Rev. B* **4** 3425
[14] Pollard R J, McCann V H and Ward J B 1983 *J. Phys. C: Sol. St. Phys.* **16** 345
[15] Szuszkiewicz B, Hennion B, Witkowska B, Łusakowska E and Mycielski A 2005 *Phys. St. Sol. (C)* **2** 1141
[16] Aplesnin S S, Ryabinkina L I, Romanova O B, Balaev D A, Demidenko O F, Yanuskevich K I and Miroshnichenko N S 2007 *Phys. Sol. St.* **49** 2080
[17] Youn S J, Min B I, Freeman A J 2004 *Phys. Stat. Sol. (B)* **241** 1411
[18] Aplesnin S S, Romanova O B, Sitnikov M N, Kretinin V V, Galyas A I and Yanushkevich K I 2018 *Sem. Sc. and Tech.* **33** 085006
[19] Kriegner D, Výborný K, Olejník K, Reichlová H, Novák V, Marti X, Gazquez J, Saidl V, Němec P, Volobuev V V, Springholz G, Holý V and Jungwirth T 2016 *Nature Comm.* **7** 11623
[20] Udod L V, Aplesnin S S, Sitnikov M N and Molokeev M S 2014 *Phys. Sol. St.* **56** 1315
[21] Aplesnin S S, Udod L V, Sitnikov M N and Shestakov N P 2016 *Ceram. Int.* **42** 5177
[22] Aplesnin S S, Ryabinkina L I, Abramova G M, Romanova O B, Kiselev N I and Bovina A F 2004 *Phys. Sol. St.* **46** 2067
[23] Aplesnin S S and Sitnikov M N 2014 *JETP Let.* **100** 95
[24] Aplesnin S S, Romanova O B and Yanushkevich K I 2015 *Phys. St. Sol. (B)* **252** 1792
[25] Aplesnin S S, Bandurina O N, Ryabinkina, L I, Romanova O B, Eremin E V, Gorev M V, Vorotynov A M, Balaev D A, Vasil'ev A D, Galyas A I, Demidenko O F, Makovetskii G I and Yanushkevich K I 2010 *Bull. Russ. Acad. Sci. Phys.* **74** 708
[26] Engle K E, Efrem D’Sa J B C, Das A and Priokar K R 2013 *JMMM* **347** 68