Structural properties of sulfides chalcogenides manganese substituted by elements with variable valency

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Abstract. The structure and transport of YbₓMn₁₋ₓS and TmₓMn₁₋ₓS sulfides (0.05≤X≤0.2) was studied in the temperature range 80-500K. The temperature ranges of local deformations and a decrease of the thermal expansion coefficient with increasing concentration X caused of anomalous compressibility in the magnetically ordered region are determined for a system doped with ytterbium. Pinning temperatures of lattice polarons are established, which are accompanied by lattice deformation and IR mode condensation for a system doped with thulium.

1. Introduction

Compounds containing rare-earth elements with variable valency such as (Sm, Yb, Ce, Eu, Tm) have a number of unique properties [1-4]. Various types of structural and phase transitions, magnetotransport effects occur in compounds based on manganese chalcogenides are observed at the changing of external conditions (temperature, pressure, composition) [5-12]. Such materials are promising from the point of view of technical applications, namely for the development and creation of the element base of RAM for high-speed electrical systems. For example, in manganese sulfides substituted by samarium ions [13], a change in the type of conductivity is observed. A large value of magnetoresistance (of the order of 100%) in the paramagnetic region at room temperatures and above was observed in manganese sulfides substituted by gadolinium ions [14]. A similar correlation of changes in the electronic and crystalline structures was observed in bismuth pyrokovskites [15,16].

The initial manganese monosulfide (MnS) in α modification is an antiferromagnetic (T_N = 150 K) acceptor-type semiconductor [17] with low carrier mobility less than 0.1 cm²/Vs [18]. Manganese monosulfide has a NaCl type FCC structure with a unit cell parameter a = 5.21 nm and undergoes a number of structural distortions at temperatures below the Néel temperature [19, 20]. Below the magnetic ordering temperature, an anisotropy of electrical resistance was found, which is two orders of magnitude larger in the (111) plane than in the (100) and depends from the magnitude of the applied magnetic field [21]. Oscillations of ions in the lattice effects on the transport [22] and magnetic [23,24] properties. Changes of the crystal structure at polymorphic transitions [25,26] causes anomalies in transport [27,28] and dielectric characteristics [29-31].

The pressure exerted by the immediate environment at substitution of manganese cations by ytterbium ions, will lead to a change of ytterbium ions valency and to the formation of a metal bond. This was observed in YbS compounds under pressure [32]. Substitution of manganese with ytterbium...
will cause an f-level shift. Whether the obtained compound remains semiconductor or becomes metallic will depend on whether the f-level is in the conduction band or remains below the bottom of the conduction band, remaining bound to the donor. The transition of an electron from the f level to the t2g state will lead to electronic degeneracy, which can be removed by spin-orbit or Jahn-Teller interaction. As a result, the appearance of electronic transitions caused by a change of the crystal symmetry is possible.

It is known that in compounds doped with rare-earth elements, including thulium and ytterbium ions along with a smooth change of the lattice parameters (lanthanoid compression), there is an anomalous interatomic distance [33]. This is explained by the fact that rare-earth metal ions are in two-valence states (or close to it). The corresponding ion has a larger ionic radius, which is reflected in an increase of the unit cell parameter, lattice deformation found in the measurement of structural, thermal and optical properties.

The aim of the work is to determine the structural and electronic phase transitions in manganese chalcogenides at the substitution by elements of ytterbium and thulium with variable valence depending from temperature and concentration.

2. Experimental results and discussions

Samples for studies of YbXMn1-XS and TmX2Mn1-XS were grown by crystallization from melt of the powder sulfides in glassy carbon crucibles and in a quartz reactor at argon atmosphere by pulling of reactor through a single-turn inductor of an high-frequency device. The synthesis of cation-substituted chalcogenide systems ReX2Mn1-XS is described in more detail in [1].

Figure 1. X-ray diffraction patterns. (a) Tm2Mn1-XS X = 0.05 and (b) YbX2Mn1-XS X = 0.05. Inset: concentration dependences of the lattice parameter of these compounds.

X-ray diffraction analysis (XRD) of TmX2Mn1-XS and YbX2Mn1-XS sulfides (0.05≤X≤0.2) was carried out on a DRON-3 installation of CuKα radiation at a temperature of 300 K before and after measurements. The X-ray analysis showed that the synthesized compounds are single-phase and have a NaCl type face-centered cubic (FCC) structure typical of manganese monosulfide. X-ray diffraction for some compositions is shown in Figures 1a, b. With an increase of cationic substitution degree, the unit cell parameter of the solid solutions TmX2Mn1-XS and YbX2Mn1-XS increases linearly in accordance with an increase of the substitution element ionic radius (r = 0.089 nm for Mn, r = 0.101 nm for Yb3+ and r = 0.116 nm for Yb2+, r = 0.102 nm for Tm3+ and r = 0.117 nm for Tm2+), which indicates the formation of solid solutions (inset to Figures 1a,b). In the case of the YbX2Mn1-XS system, the asymptotic elongation of the unit cell value a(X) to X = 1 gives the parameter value a(X = 1) = 0.559 nm, which is 2.4% less than the value as for YbS. It is known that compression of the lattice by 4% under pressure [32] leads to a spin transition of the ytterbium ion from the singlet state with J = 0 to J = 7/2, S = 1/2. It follows from this that the chemical pressure created by manganese ions is insufficient for the electronic transition from Yb2+ to Yb3+.
Figure 2. The temperature dependence of the thermal expansion coefficient $\alpha$ (T). (a) Tm$_x$Mn$_{1-x}$S, $X = 0.05(1), 0.1(2), 0.15(3)$, (b) Yb$_x$Mn$_{1-x}$S, $X = 0.05(1), 0.1(2), 0.2(3)$.

The thermal expansion coefficient was measured to analyze the effect of substitution by thulium and ytterbium ions on the structural characteristics, in particular, on the change of the sample size (anomalous compressibility), and also to determine local deformations from temperature. The relative variation in the sample volume with temperature was measured on a DIL–402C dilatometer. Minima were found in the temperature range 260–270 K and 485–495 K (Figure 2a) for the system Tm$_x$Mn$_{1-x}$S, with $X = 0.05; 0.1; 0.15$. It should be noted that the magnitude of these minima increases with increasing of substitution concentration, and the change of sample volume decreases at these temperatures. It has been suggested that the slowdown is associated with the contribution of lattice polarons above the Debye temperature $T_D = 250$ K. Small minima were detected on the $\alpha$ (T) curve in the vicinity of 355–370 K due to the formation of hole-type optical polarons. Local lattice deformation is caused by a structural transition from the low-symmetry state to the cubic phase in the lattice region containing thulium ions at 490 K.

The results of studies of the thermal expansion coefficient $\alpha$ are presented in figure 2b for the system Yb$_x$Mn$_{1-x}$S (0.05$\leq X \leq$0.2). The dependence $\alpha$ (T) shows anomalies in the temperature range of the magnetic phase transition $110K$ $\leq$ T $\leq$ $140K$. With increasing ytterbium concentration, the value of $\alpha$ for all (X) decreases and does not change only in the paramagnetic phase. This is explained by the fact that, upon transition to a magnetically ordered region, the lattice begins to abnormally compress as a result of magnetoelastic interaction. The magnetoelastic interaction can be presented as $\beta U <S_iS_{i+h}>$, where $\beta$ is the parameter of this interaction, and $U$ is the relative displacement of the ions. In the approximation of the molecular field the minimum of intrinsic energy $\frac{dE}{dU}$:

$$E = -J(S_iS_{i+h}) - \beta U(S_iS_{i+h}) + \frac{1}{2}kU^2$$

where $J$ is the exchange interaction, $k$ is the elastic constant, and $z$ is the number of interacting ion spins that determine the displacement $U = \beta <S_iS_{i+h}>/k$. Lattice compression in the magnetically ordered region is most likely due to two factors: a change in the elastic parameters $\beta/k$ and a spin correlation function $<S_iS_{i+h}>$. If the behavior of the effective exchange and lattice parameter in the Yb$_x$Mn$_{1-x}$S solid solution at the change of the ytterbium ions concentration is known, then we can estimate the change of the magnetoelastic interaction parameter. The parameter $\beta = \frac{dJ}{dU}$ characterizes the change of the exchange value with the lattice parameter, and the change of exchange is proportional to the Néel temperature: $\frac{dJ}{dx} \sim \left(\frac{2}{3}S(S+1)z\right)^{-1}\frac{dT_N}{dx} = 0.01$. As an increase of the substitution concentration, the lattice parameter increases: $\frac{dx(x)}{dx} = 0.35$, and the magnetoelastic interaction parameter decreases and becomes $0.3%$ ($\frac{d\beta}{dx} = 0.0032$). The elastic modulus of ytterbium
sulfide is approximately 10% greater than the elastic modulus of the starting manganese monosulfide.

The coefficient of thermal expansion was determined by the formula:

\[ \alpha(T) = \frac{du(T)}{dT} = \frac{\delta S_{i+1} d\langle \frac{f}{2} \rangle}{d\langle \frac{f}{2} \rangle} + \frac{\beta d(S_{i+1}^h)}{k} \approx \frac{\beta d(S_{i+1}^h)}{k} \] (2)

The temperature dependence of the thermal expansion coefficient is associated with a change of the spin-spin correlation function as a function of temperature. Two maxima on the \( \alpha(T) \) curve relate to the inflection points of the function \( \langle S_i S_{i+h} \rangle \) detected at \( T = 105 \) K and \( T_N = 126 \) K. At a concentration \( X > X_c \) (\( X_c \) is the percolation concentration), the dispersion of the distribution function of the local exchange fields increases, and the spin-spin correlation function decreases. The result of this is the detection of a diffuse maximum on the dependence \( \alpha(T) \) in the magnetic phase transition region.

Figure 3. The temperature dependences of the intensity of the IR spectra. (a) \( \text{Yb}_{0.15}\text{Mn}_{0.85}\text{S} \) and (b) \( \text{Tm}_{0.15}\text{Mn}_{0.85}\text{S} \).

Substitution of \( \text{Mn}^{2+} \) with \( \text{Yb}^{2+} \delta^+ \) ions will lead to electron doping and to the formation of the degeneracy of the \( t_{2g} \) shell. This degeneracy can be removed due to the Jahn-Teller effect, or by spin-orbit interaction. The distortion of the octahedra as a result of the Jahn-Teller effect can be observed in the IR absorption spectra shown in Figures 3a. IR spectra were obtained in the frequency 450 cm\(^{-1}\) – 7500 cm\(^{-1}\) and temperatures range 80–500 K on FSM2202 IR Fourier spectrometer. Two absorption peaks at \( \omega_1 = 953 \) cm\(^{-1}\) and \( \omega_2 = 994 \) cm\(^{-1}\) were detected in the \( \text{Yb}_{0.15}\text{Mn}_{0.85}\text{S} \) system. The first peak at the frequency \( \omega_1 \) disappears in the temperature range \( T < 200 \) K, and the intensity of the second peak decreases several times and disappears at \( T = 400 \) K. The frequencies \( \omega_1 \) and \( \omega_2 \) shift by 3 and 12 cm\(^{-1}\), respectively with increasing temperature. The formation of two lines in the IR absorption spectra is also associated with a spin – orbit interaction of the order of 40 cm\(^{-1}\). The dynamic Jahn-Teller effect is realized in the temperature range 200–270 K. At \( T > 270 \) K, the Jahn-Teller effect transforms into uncorrelated static deformations of the octahedral, which leads to the disappearance of the second peak of IR absorption.

The model of lattice polarons detected in the \( \text{Tm}_2\text{Mn}_{1-X}\text{S} \) system as a result of studying the thermal expansion coefficient is confirmed by IR spectra. Two frequencies were found at which the intensity decreases with increasing temperature (Figures 3b, c). The absorption spectral line in the vicinity of the frequency \( \omega_1 = 3116 \) cm\(^{-1}\) disappears at the temperature range 240–270 K for all compositions (0.05\( \leq X \leq 0.2 \)). The lattice polaron below the Debye temperature \( T_D = 255 \) K is pinned at anion vacancies for manganese sulfide. The IR mode at a frequency \( \omega_1 = 3116 \) cm\(^{-1}\) corresponds to the energy of electron transfer from a localized polaron to a vacancy. Interaction with acoustic phonons leads to redistribution of polarons. The intensity decreases proportionally to the density of acoustic phonons. This can be represented as a function \( I_{ab} \sim 1 - A \ T \), which satisfactorily describes the experimental results with a critical temperature for the separation of polarons from defects found in
the lattice. The wide maximum of absorption intensity found at a frequency $\omega_1 = 1240$–$1320 \text{ cm}^{-1}$ for $X = 0.15$ is caused by pinning of optical polarons at the Mn – Tm interface. The polaron exchange interaction with localized manganese spins exceeds the energy of the Coulomb interaction with the charged interface in the magnetically ordered region. Such an interaction leads to the separation and disappearance of the polaron – charged impurity complex. The delocalization of current carriers from the Mn-Tm boundary in the manganese subsystem is described by a power-law dependence $I = A (1 - T/T_c)^{0.85}$ with a temperature $T_c = 350 \text{ K}$. The observed increasing of the absorption intensity with increasing temperature to $500 \text{ K}$ at $450 \text{ cm}^{-1}$ is associated with a structural transition.

3. Conclusion
Substitution of manganese ions by ytterbium and thulium ions with a variable valency leads to a change in the structural characteristics that reflected in measuring of the thermal expansion coefficient and IR spectra. It was found, the thermal expansion coefficient of the samples decreases in the antiferromagnetic region at increasing ytterbium concentration. A linear changing of the sample size is explained by the weakening of spin correlations in the solid solution. Two peaks, in the coefficient of thermal expansion, arise due to the inhomogeneous distribution function of the local exchange fields. Two electronic transitions were found from the IR spectra that disappear at $200 \text{ K}$ and at $400 \text{ K}$, respectively. The transitions are caused by a sequential increase of the octahedron symmetry and the splitting of the $t_2g$ states of the ions. The correlation between the temperatures of lattice deformation and the IR mode condensation was established for samples doped with thulium in Tm$_x$Mn$_{1-x}$S system. The lattice deformation is due to the localization of electrons on the lattice defects and charged centers as a result of the interaction of electrons with the lattice, acoustic and optical modes of lattice vibrations at decreasing temperature.

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References
[1] Aplesnin S S, Ryabinkina L I, Romanova O B, Sokolov V V, Pichugin A Y, Galyas A I, Demidenko O F, Makovetskii G I and Yanushkevich K I 2009 Phys. Sol. St. 51 698
[2] Aplesnin S S, Romanova O B, Gorev M V, Velikanov D A, Gamzatov A G, Aliev A M 2013 J. Phys. Cond. Matt. 25 025802
[3] Aplesnin S S, Sitnikov M N, Romanova O B, Pichugin A Yu 2016 Phys. St. Sol. B 253 1771
[4] Alanko G A, Butt D P 2014 J. American Ceram. Soc. 97 2357
[5] Aplesnin S S, Romanova O B, Gorev M V, Vasil’ev A D, Demidenko O F, Makovetskii G I, Yanushkevich K I 2012 Phys. Sol. St. 54 1374
[6] 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, Bandurina O N 2008 JETP 106 765
[7] Petrakovskii G A, Ryabinkina L I, Velikanov D A, Aplesnin S S, Abramova G M, Kiselev N I, Bobina A F 1999 Phys. Sol. St. 41 1520
[8] Aplesnin S S, Romanova O B, Korolev V V, Sitnikov M N, Yanushkevich K I 2017 J. Appl. Phys. 121 7
[9] Aplesnin S S, Romanova O B., Yanushkevich K I 2015 Phys. St. Sol. B 252 1792
[10] Aplesnin S S, Romanova O B, Sitnikov M N, Kretinin V V, Galyas A I, Yanushkevich K I 2018 Sem. Sc. and Tech. 33 085006
[11] Aplesnin S S, Ryabinkina L I, Romanova O B, Gorev M V, Balaev A D, Eremin E V, Bandurina O N 2009 Bulletin of the Russian Academy of Sciences: Physics 73 965
[12] Petrakovskii G A, Loseva G V, Ryabinkina L I, Aplesnin S S 1995 JMMM 140-144 147
[13] Aplesnin S S, Romanova O B, Har’kov A M, Balaev D A, Gorev M V, Vorotinov A M, Sokolov V V, Pichugin A Yu 2012 Phys. St. Sol. B 249 812
[14] Aplesnin S S, Sitnikov M N 2014 JETP Let. 100 95
[15] Udod L V, Aplesnin S S, Sitnikov M N, Molokeev M S 2014 *Phys. Sol. St.* **56** 1315
[16] Aplesnin S S, Udod L V, Sitnikov M N, Shestakov N P 2016 *Ceram. Int.* **42** 5177
[17] Heikens H H, Wiegers G A and van Bruggen C F 1977 *Sol. St. Com.* **24** 205
[18] Nagaev E L 1996 *Phys. Usp.* **39** 781
[19] Aplesnin S S, Petrikovskii G A, Ryabinkina L I, Abramova G M, Kiselev N I, Romanova O B 2004 *Sol. St. Com.* **129** 195
[20] Aplesnin S S, Ryabinkina L I, Abramova G M, Romanova O B, Vorotynov A M, Velikanov D A, Kiselev N I, Balalev A D 2005 *Phys. Rev. B* **71** 125204
[21] Aplesnin S S, Ryabinkina L I, Abramova G M, Romanova O B, Kiselev N I, Bovina A F 2004 *Phys. Sol. St.* **46** 2067
[22] Aplesnin S S 2003 *JETP* **97** 969
[23] Aplesnin S S 2000 *Phys. Rev. B* **61** 6780
[24] Aplesnin S S 1998 *J. Phys. Cond. Matt.* **10** 10061
[25] Romanova O B, Aplesnin S S, Sitnikov M N, Kharkov A M, Masyugin A N, Yanushkivich K I 2019 *Sol. St. Com.* **287** 72
[26] Udod L V, Aplesnin S S, Sitnikov M N, Romanova O B, Molokeev M N 2019 *J. Alloy Comp* **804** 281
[27] Romanova O B, Aplesnin S S, Udod L V, Sitnikov M N, Kretinin V V, Yanushkevich K I Velikanov D A 2019 *J. Appl. Phys.* **125** 175706
[28] Aplesnin S S, Udod L V, Sitnikov M N, Molokeev M S, Tarasova L S, Yanushkevich K I 2017 *Phys. Sol. St.* **59** 2268
[29] Aplesnin S S, Udod L V, Sitnikov M N 2018 *Ceram. Int.* **44** 1614
[30] Aplesnin S S, Udod L V, Sitnikov M N, Kretinin V V, Molokeev M S, Mironova-Ulmane N 2018 *Mater. Res. Express.* **5** 115202
[31] Aplesnin S S, Kretinin V V, Begisheva O B 2019 *Phys. Sol. St.* **61** 1379
[32] Matsunami M, Okamura H, Ochiai A, Nanba T 2009 *Phys. Rev. Lett.* **103** 237202
[33] Aurelio A, Guillermet F 1999 *J. Appl. Phys.* **292** 31