Physics of the Solid State, 2022, Vol. 64, No. 4

05

Electrical and magnetic properties of vanadium diselenide intercalated with chromium atoms

© *E.M. Sherokalova, N.V. Selezneva, V.G. Pleshchev*

Institute of Natural Sciences and Mathematics, Ural Federal University,
Yekaterinburg, Russia

E-mail: v.g.pleshchev@urfu.ru

Received December 17, 2021
Revised December 17, 2021
Accepted December 27, 2021

The study of the structural characteristics, electrical and magnetic properties was carried out on synthesized samples of vanadium diselenide intercalated with chromium atoms. Structural studies have shown a decrease in the symmetry of the crystal lattice from hexagonal to monoclinic with an increase in the concentration of intercalated atoms, caused by their ordering in the Van der Waals gap. In this case, a change in the resistive state occurs in samples of different compositions, which are characterized by opposite thermal coefficients of electrical resistance. The values of the effective magnetic moments of chromium ions in Cr_xVSe_2 decrease in comparison with the spin characteristics with an increase in the chromium content and their change correlate with the concentration dependence of the parameter c of the unit cell. At low temperatures for compositions $x > 0.2$, the compounds undergo a transition to the state of a spin glass with a critical temperature of up to 30 K.

Keywords: vanadium diselenide, chromium, intercalation, electrical resistance, magnetic susceptibility, spin glass.

DOI: 10.21883/PSS.2022.04.53498.256

1. Introduction

Layered transition metals dichalcogenides (LTMDs) with the common formula TX_2, where T is transition metal of groups IV, V, X is chalcogen) have a pronounced quasi-two-dimensional pattern of the crystalline structure, which is due to the so-called „van der Waals gap" (VDW) between three-layer blocks („sandwiches") $X-T-X$, where atoms of different elements or even entire molecules can be embedded (intercalated) [1–2].

The main motive of the crystalline structure is usually retained when foreign atoms are embedded into LTMDs. Nevertheless, different concentrations of intercalated atoms in this compounds correspond to different structural modifications caused by a different number of TX_2 layers in a unit cell, as well as with ordering of vacancies and interstitial atoms in VDW gaps. Ordering in the intercalant sublattice, in addition to unit cell volume increase, is accompanied by a reduction of its symmetry [3–5]. Previous studies have shown that physical properties of compounds, obtained by intercalation with atoms of $3d$-transition elements, differ significantly from the properties of initial TX_2 compounds. Additional interactions of interstitial atoms with matrix atoms lead to a crystal lattice deformation, change in electrical and magnetic properties of intercalated materials and formation of various magnetic states [6,7].

The most well-studied among such compounds are titanium dichalcogenides and intercalates on their basis, the crystalline structure of which is represented by one TX_2 layer per unit cell. Several dichalcogenides of elements of group 5 and vanadium diselenide in particular, have the same structure. This compound, like $TiSe_2$, experiences a transition to a state with a charge-density wave, though at lower temperatures (110 K) [3,8].

Intercalation of VSe_2 with atoms of other elements, like in titanium diselenide-based compounds, as well as self-intercalation processes that give rise to crystalline structure distortion, suppress this structural transformation. Thus, for instance, self-intercalation in vanadium diselenide V_xVSe_2 suppresses the CDW wave already at $x > 0.01$, and in the Fe_xVSe_2 this happens at $x > 0.033$ [9,10].

Despite the similar crystalline structures of different LTMDs, analysis of mechanisms of formation of intercalated compounds' physical properties must take into account not only the different nature and electronic structure of $3d$-elements' interstitial atom, but also the typical features of the initial dichalcogenides used for intercalation. Thus, for instance, an antiferromagnetic state was found in the Cr_xTiSe_2 system at $x = 0.33$, and ferromagnetic alignment forms in Cr_xTiTe_2 and Cr_xMoSe_2 [11,12].

In this respect, the present paper is dedicated to an integrated study of the structural features, electric and magnetic properties of vanadium diselenide intercalated with chromium atoms.

2. Experiment

Polycrystalline samples of Cr_xVSe_2 were prepared by solid-state synthesis in evacuated quartz ampules in two stages. The first stage was the synthesis of samples of the VSe_2 binary compound, which were used later as intercalation hosts. The second stage was the preparation of samples of intercalated compounds by mixing the obtained hosts with the necessary amount of chromium according to reaction $x\mathrm{Cr} + \mathrm{VSe}_2 = \mathrm{Cr}_x\mathrm{VSe}_2$ $(0 \leq x \leq 0.33)$. Synthesis temperature at each stage was 800°C and holding time was at least 100 h. Rubbing and pressing of the obtained preparations and a second diffusion annealing were performed at each stage after the first annealing. If necessary, the operations were repeated. This procedure has been successfully used in synthesis of other intercalated systems [5–7]. Its advantage is the more probable prevention of the formation of binary chalcogenides of both metals in case of direct synthesis from the initial elements. Phase composition check and determination of structural characteristics were performed using a Bruker D8 Advance X-ray diffractometer and the method of full-profile analysis of radiography data.

Electrical resistance was measured using the standard four-probe method in the temperature range of $100-300$ K. Magnetization was measured using a SQUID-magnetometer (MPMS) in the temperature range of $2-300$ K and magnetic field range up to 60 kOe.

The radiography qualification has confirmed the single phase characteristic of the obtained samples, and the unit cell parameters were determined. It has been established that the X-ray images for the $\mathrm{Cr}_x\mathrm{VSe}_2$ samples with a small chromium content $(0.05 \leq x \leq 0.2)$ are indexed within the framework of a trigonal system with space group $P\bar{3}m1$, corresponding to the initial VSe_2. Ordering of chromium atoms was found when chromium content in the samples of $\mathrm{Cr}_{0.25}\mathrm{VSe}_2$ and $\mathrm{Cr}_{0.33}\mathrm{VSe}_2$ increased. Their X-ray images were indexed in a monoclinic system $(\mathrm{SG} = I2/m)$ with the unit cell parameters $2\sqrt{3}a_0 \times 2a_0 \times 2c_0$, where a_0 and c_0 are the unit cell parameters for the initial vanadium diselenide.

3. Results

The electrical resistance measurements have revealed that the temperature dependences of samples with different chromium contents are different in nature. Dependence $\rho(T)$ for VSe_2 is strictly linear, and we can conclude that the charge carrier scattering is chiefly electron-phononic. The electrical resistance value increases when chromium is intercalated $(x = 0.05$ and $x = 0.1)$. Magnitude ρ also increases with temperature rise, but dependence $\rho(T)$ is not linear anymore and indicates that an additional mechanism occurs in addition to phonon scattering. These dependences to a large extent correspond to $\rho(T) = \rho_0 + aT^m$, where $m > 1$. The determined (by approximation) quantities m for these two samples are 1.4 and 1.7 respectively, which suggests that the nature of an additional contribution to electrical resistance can be associated with electron-electron scattering, since this mechanism, according to the current concepts, may lead to dependence $\rho(T) \propto T^2$ [13]. Magnitude of the temperature-independent term ρ_0 in the equation for $\rho(T)$ must represent the resistance caused by presence of intrinsic structural defects and impurities, being interstitial chromium atoms (ions) (Fig. 1). Estimation of this contribution to electrical resistance yielded the values equal to $1.05 \cdot 10^{-5}$ and $1.93 \cdot 10^{-5}\,\Omega \cdot \mathrm{m}$. The almost twofold increase of ρ_0 corresponds to the same increase of chromium in the samples with $x = 0.05$ and $x = 0.1$. Dependence $\rho(T)$ in case of chromium content increase at $x \geq 0.2$ undergoes qualitative changes and is characterized by a negative temperature coefficient. If this dependence is considered as a manifestation of the activation process, our estimates of the activation energy for these samples yielded the values of 2 to 5 meV, which defines rather a weak change of ρ in the given temperature range. A transient case is observed for the $\mathrm{Cr}_{0.15}\mathrm{VSe}_2$ composition, where the sign of the temperature coefficient for electrical resistance changes as temperature rises (Fig. 2). Fig. 2 also gives a summary concentration dependence of electrical resistance of the $\mathrm{Cr}_x\mathrm{VSe}_2$ samples at two temperatures. The crosshatched region, containing the composition with $x = 0.15$, is the probable region of chromium atom contents, within which the temperature dependence of electrical resistance changes in nature. The observed change in the resistive state can be caused by the above-mentioned processes of ordering of intercalated atoms and the associated changes in the compounds' electronic structure [14].

When chromium content increases from $x = 0.2$ to $x = 0.33$, quantity ρ increases, like for smaller concentrations $(x = 0.05$ and $x = 0.1)$. Thus, we should conclude that, despite the possible manifestation of the activation process in structurally ordered samples, the overall concentration dependence of electrical resistance depends on increasing charge carrier scattering with chromium content increase in $\mathrm{Cr}_x\mathrm{VSe}_2$.

The temperature dependences of magnetic susceptibility (χ) of $\mathrm{Cr}_x\mathrm{VSe}_2$ measured in magnetic field $H = 10$ kOe are shown in Fig. 3. These dependences for samples with $x = 0$, 0.05, 0.1 in the whole temperature region demonstrate a monotonic decrease of susceptibility under heating and susceptibility increase when x increases. The samples with $x = 0.2$, 0.25, 0.33 have disrupted monotonic dependences $\chi(T)$ in the low temperature region, while magnetic susceptibility magnitude decreases with when x increases. The temperature dependences of magnetic susceptibility of the intercalated compounds in the temperature range of $70-300$ K were processed according to the Curie–Weiss law as $\chi = \chi_0 + C/(T - \Theta)$, where C — Curie constant, Θ — Curie–Weiss temperature, χ_0 — temperature-independent contribution that comprises the diamagnetism of filled electronic shells and electron gas paramagnetism. The table

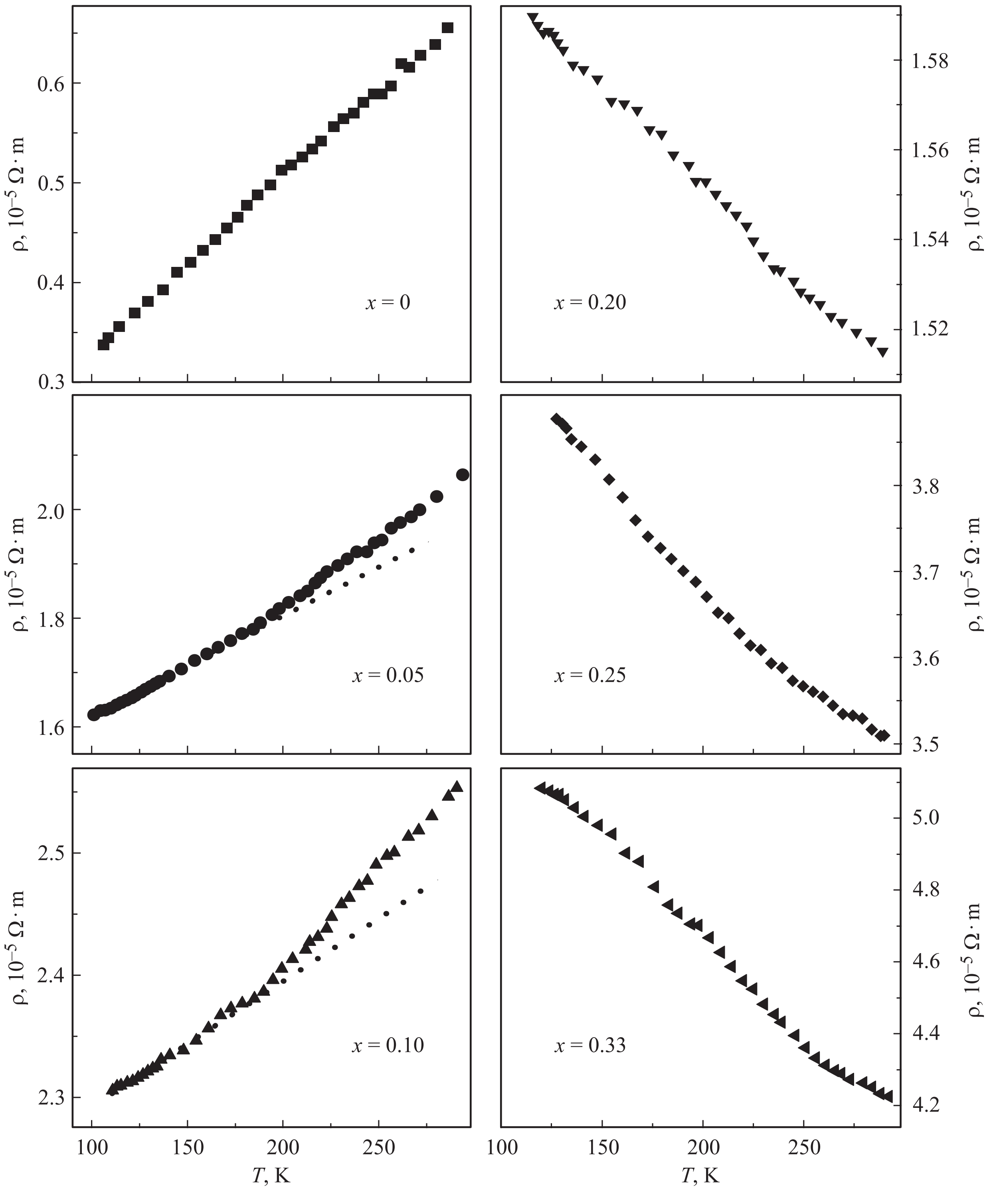

Figure 1. Temperature dependences of electrical resistance of the Cr_xVSe_2 samples.

gives the values of these parameters obtained by approximation.

Since the V^{4+} ion in these compounds, like the chromium ion, can have an uncompensated magnetic moment, the effective magnetic moments were determined from the experimental data per formula unit of these compounds.

It is seen that chromium intercalation leads to an increase of μ_{eff}/f.u., determined from the experiment and calculated per formula unit of the compound.

Since the magnitude of these moments is determined simultaneously by the contribution of the host and by intercalated chromium ions, the experimental value of

Values of temperature-independent contribution χ_0, Curie–Weiss temperature Θ, effective magnetic moments of the formula unit of the Cr_xVSe_2 compounds μ_{eff},/f.u. and chromium ions μ_{eff}/Cr depending on chromium content

x	χ_0, 10^{-6} emu/(g · Oe)	Θ, K	μ_{eff},/f.u., μ_B	μ_{eff}/Cr, μ_B
0	1.3	−0.5	0.46	0
0.05	1.4	−0.8	0.85	3.78
0.1	1.6	−6.2	1.20	3.75
0.2	2.4	−10	1.51	3.39
0.25	4.4	−24	1.45	2.86
0.33	3.1	−16	1.55	2.67

μ_{eff}/f.u. can be presented as an equation from which we determined the effective magnetic moments for the chromium ions in the Cr_xVSe_2 compounds

$$(\mu_{eff}^{exp})^2 = (\mu_{eff}^{VSe_2})^2 + x \cdot \mu_{eff}^{Cr})^2,$$

where the value, obtained for the initial host, was adopted for $\mu_{eff}^{VSe_2}$. The effective magnetic moments per chromium ion, determined in this way, are given in the table. The decrease of these values as compared to the spin moment for a free Cr^{3+} ion ($3.87\,\mu_B$) indicates that 3*d*-electrons of chromium undergo significant hybridization with VSe_2 states. This hybridization also conditions a decrease of the unit cell parameter *c* in the direction perpendicular to the layer plane, with an increase of chromium content which was found in the course of the X-ray studies. Fig. 4 shows a correlation between the changes of μ_{eff}/Cr and parameter c_0.

Magnetic susceptibility in the low temperature region was additionally studied in the ZFC and FC modes using lower magnetic field values (100 Oe). The samples with $x = 0.2$, $x = 0.25$ and $x = 0.33$ had the maxima at the temperatures of 8, 13 and 30 K respectively, as well as a hysteresis below these temperatures during measurements in the ZFC and FC modes (Fig. 5). This may mean that a state of the spin or cluster glass type forms below the critical temperature. Negative values of Curie–Weiss temperature, as well as magnetic susceptibility decrease in the low temperature region with an increase in the content of magnetoactive atoms suggests the presence of antiferromagnetic interactions in the Cr_xVSe_2 system. This is also indicated by the field dependences of magnetization shown in Fig. 3 and demonstrating the absence of saturation up to the magnetic field of 6 kOe.

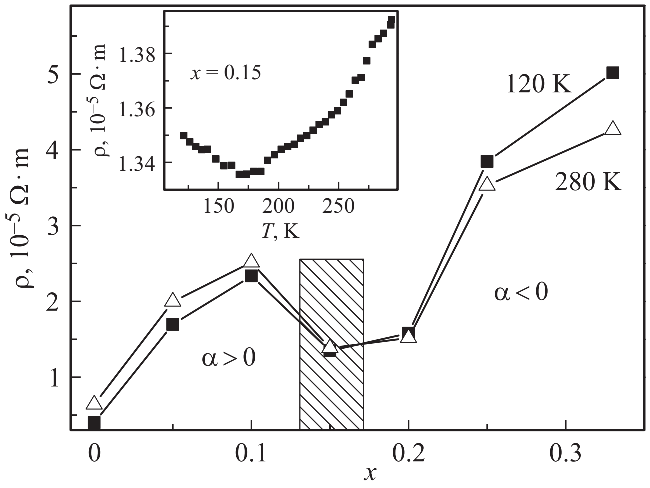

Figure 2. Concentration dependences of electrical resistance in the Cr_xVSe_2 system and temperature dependence of electrical resistance of $Cr_{0.15}VSe_2$ (in the insert).

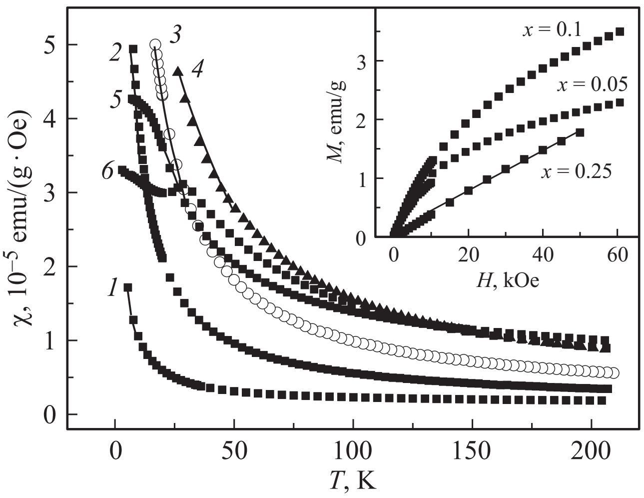

Figure 3. Temperature dependences of magnetic susceptibility of the Cr_xVSe_2 samples at $x = 0$ (*1*), $x = 0.05$ (*2*), $x = 0.1$ (*3*), $x = 0.2$ (*4*), $x = 0.25$ (*5*), $x = 0.33$ (*6*). The insert shows the field dependences of magnetization for the Cr_xVSe_2 compounds at $T = 2$ K.

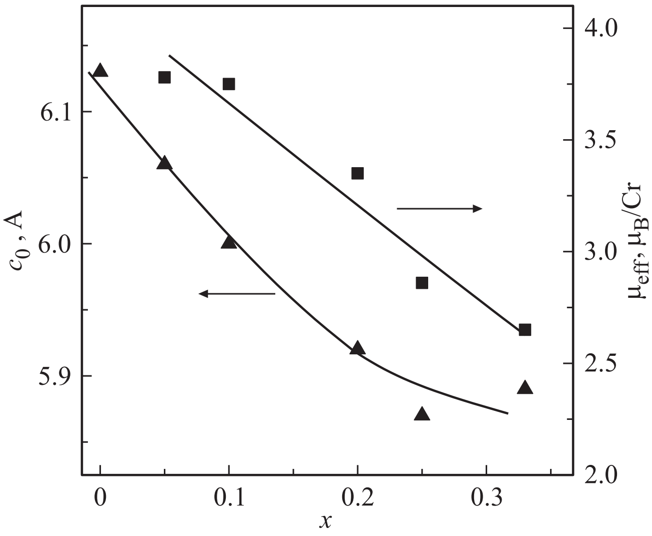

Figure 4. Concentration dependences of unit cell parameter c_0 and effective magnetic moment per chromium ion in Cr_xVSe_2.

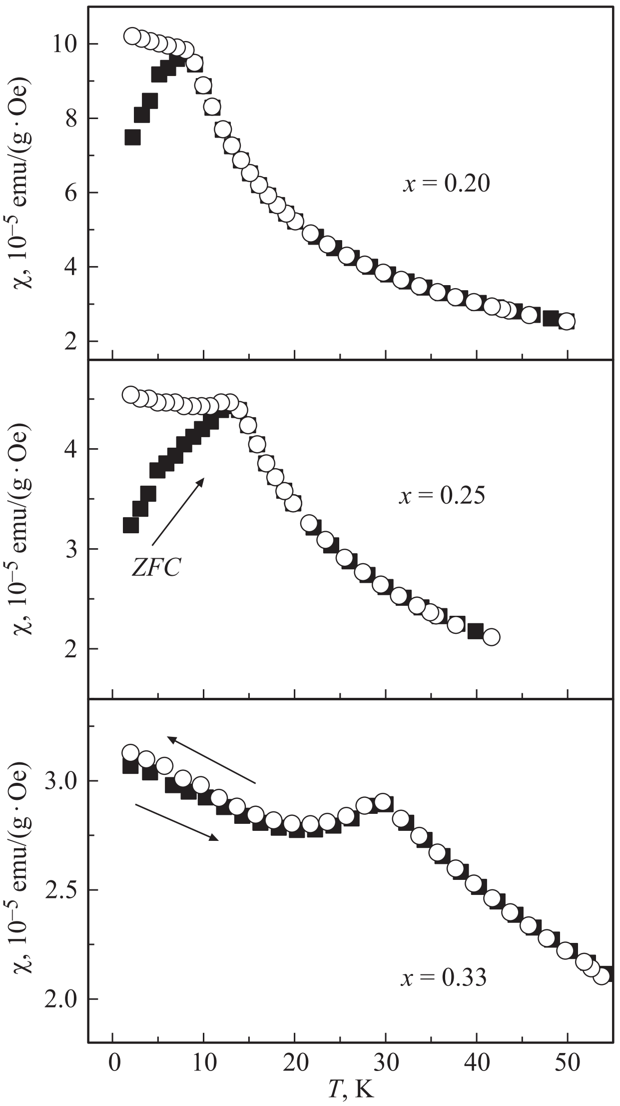

Figure 5. Temperature dependences of magnetic susceptibility of Cr_xVSe_2 in ZFC and FC modes ($H = 100\,Oe$).

4. Conclusion

The performed studies and their results indicate a relationship between structural transformations during intercalation of vanadium diselenide with chromium and the formed physical properties. An increase of chromium content in Cr_xVSe_2 is accompanied with an ordering of chromium and vacancies in VDW-gaps and a reduction of unit cell symmetry from trigonal to monoclinic. This ordering and the associated electronic structure transformation manifests itself in a resistive state change that consists in a sign change of the electrical resistance temperature coefficient.

Effective magnetic moments of chromium ions were determined from the data on temperature dependences of magnetic susceptibility with consideration of the possible contribution from the VSe_2 parent host. It was shown that magnitudes of μ_{eff}/Cr for the compounds with $x = 0.05$ and $x = 0.1$ virtually match the spin moment of Cr^{3+} ions ($3.87\,\mu_B$), while it decreases to $2.67\,\mu_B$ when chromium content increases to $x = 0.33$. A comparison of concentration dependences μ_{eff} and unit cell parameter c_0 allow for making a conclusion on delocalization of chromium $3d$-electrons and their hybridization with electron states of the parent matrix. The existence of spin-glass states with an increasing magnetic transformation temperature up to 30 K for $Cr_{0.33}VSe_2$ was found in the low temperature region with chromium content $x \geq 0.2$. Magnetic susceptibility decrease with increase of chromium content, negative values of Curie–Weiss temperature and absence of saturation on field dependences of magnetization up to $H = 60\,kOe$ indicate the antiferromagnetic nature of interaction in the temperature region of the spin-glass state. Thus, the obtained data shows that a long-range magnetic order does not establish in the Cr_xVSe_2 system with chromium concentrations up to $x = 0.33$, as distinct from such chromium-containing systems as Cr_xTiSe_2, Cr_xTiTe_2 or Cr_xMoSe_2 [6,11,12]. This emphasizes the important role of LTMD nature in the formation of intercalated compounds' physical properties.

Funding

This study was funded by the Ministry of Science and Higher Education of the Russian Federation (project No. FEUZ-2020-0054).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] W. Choi, N. Choudhary, J. Park, G.H. Ha, Y.H. Lii, D. Akinwande. Mater. Today **20**, *3*, 116 (2017). doi: 10.1016/j.mattod.2016.10.002

[2] L.A. Chernozatonsky, A.A. Artyukh UFN **188**, *1*, 3 (2018) (in Russian). doi: 10.3367/UFNr.2017.02.038065

[3] A. Hayashi, Y. Ueda, K. Kosuge Mater. Res. Bull. **24**, *7*, 825 (1989). doi: 10.1016/0025-5408(89)90045-7

[4] A.S. Shkvarin, Y.M. Yarmoshenko, A.I. Merentsov, I. Píš, F. Bondino, E.G. Shkvarina, A.N. Titov. Inorganic Chem. **57**, *9*, 5544 (2018). doi: 10.1021/acs.inorgchem.8b00511

[5] N.V. Selezneva, V.G. Pleshchev, N.V. Baranov. FTT **56**, *12*, 2293 (2014) (in Russian).

[6] N.V. Baranov, V.G. Pleshchev. Magnetic Properties of Layered Titanium Dichalcogenides Intercalated with 3d- and 4d-Metals. In: Handbook of Material Science Research / Eds Ch. René, E. Turcotte. Nova Science Publishers (2010). P. 295–322.

[7] V.G. Pleshchev, A.N. Titov, S.G. Titova. FTT **45**, *3*, 409 (2003) (in Russian).

[8] C.S. Yadav, A.K. Rastogi. Solid State Commun. **150**, *13–14*, 648 (2010). doi: 10.1016/j.ssc.2009.12.026

[9] N.V. Selezneva, E.M. Sherokalova, V.G. Pleshchev, V.A. Kazantsev, N.V. Baranov. J. Phys.: Condens. Matter **28**, 315401 (2016). doi: 10.1088/0953-8984/28/31/315401

[10] C.S. Yadav, A.K. Rastogi. J. Phys.: Condens. Matter **20**, *46*, 465219 (2008). doi: 10.1088/0953-8984/20/46/465219

[11] N.V. Baranov, V.G. Pleshchev, N.V. Selezneva, E.M. Sherokalova, A.V. Korolev, V.A. Kazantsev, A.V. Proshkin. J. Phys.: Condens. Matter **21**, *50*, 506002 (2009).
doi: 10.1088/0953-8984/21/50/506002

[12] V.G. Pleshchev, N.V. Selezneva. FTT **61**, *3*, 472 (2019) (in Russian). doi: 10.21883/FTT.2019.03.47238.274

[13] F. Blatt. Physics of electronic conduction in solids. Mir, M. (1971). 470 p. (in Russian).

[14] A.H. Reshak, S. Auluck. Physica B: Condens. Matter **349**, *1–4*, 310 (2004). doi: 10.1016/j.physb.2004.03.31314