Physics of the Solid State, 2024, Vol. 66, No. 9

03,05,10

Electrical and magnetic properties intercalated phases in the Fe-MoS_2 system

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Received May 26, 2024
Revised July 19, 2024
Accepted July 22, 2024

In this work, samples of molybdenum disulfide intercalated with iron atoms with different concentrations by the developed technology were synthesized for the first time and the results of original studies of electrical and magnetic properties of intercalated iron-containing materials depending on composition and temperature were presented. The obtained data demonstrate the activation character of conductivity in the system of intercalated Fe_xMoS_2 phases with a possible change in the mechanism of conductivity associated with the increase in the concentration of iron in the samples. The possibility of realization of antiferromagnetic state in compounds with different iron content based on the character of temperature dependences of magnetic susceptibility, negative values of paramagnetic Curie temperature and the form of temperature dependences of effective magnetic moments is shown.

Keywords: molybdenum disulfide, iron, electrical resistance, magnetic susceptibility, effective magnetic moment.

DOI: 10.61011/PSS.2024.09.59212.138

1. Introduction

Dichalcogenides of transition metals with general formula TX_2 (T — transition metal of 4, 5, 6th groups of Periodic Table, X — S, Se, Te) attracted great interest in recent years due to their use in Van der Waals heterostructures [1–3]. Due to two-dimensional nature of the crystalline structure TX_2, into the interlayer space the embedding of other element atoms is possible, which ensures the properties of such materials changing in wide range [4–8].

Among them, an apparent place belongs to molybdenum dichalcogenides. So, for example, molybdenum disulphide MoS_2 is an advanced material not only due to its tribological characteristics, but also as a basis for electronic devices [2,3]. Since molybdenum dichalcogenides frequently named as graphene-like materials due to easy decouping of individual layers, many studies relate to obtaining and study of physical properties of such monolayers [9,10].

Unlike dichalcogenides of 4th group o periodic Table the molybdenum disulphide can have different structural modifications (polytypes). Additionally to unstable modification 1T-MoS_2, we have interest to such phases as 2H-MoS_2 and 3R-MoS_2, that differ by position of atoms and number of layers of MoS_2 in lattice cell. Modification 2H-MoS_2 is described under framework of hexagonal structure. The lattice cell of this compound contains two layers of MoS_2 with trigonal prismatic environment of molybdenum atoms. The polytype 3R-MoS_2 has rhombohedral structure, spatial group R3m. Its three-layer packing leads to that the lattice cell parameter along axis increases as compared to 2H-MoS_2 by about one-and-a-half times.

The available in literature data show that properties of this material depend on number of MoS_2 layers. When the bulk crystals of molybdenum disulphide are semiconductors with indirect band gap with width of 1.2 eV [11], for MoS_2 monolayer splitting by crystal field of d-orbitals leads to direct band gap 1.8 eV [9].

The magnetic properties of bulk compounds of molybdenum disulphide, intercalated by transition 3d-elements with general formula $M(3d)Mo_2S_4$ ($M =$ Ni, V, Cr, Fe, Co), were studied in paper [12]. Based on magnetic and neutron diffraction data in $FeMo_2S_4$ the antiferromagnetic state was determined at temperatures below 110 K. At the same time there are notifications that the synthetized MoS_2, monolayers doped with iron demonstrate ferromagnetic properties and ferromagnetism even at 300 K with the characteristic loop of magnetic hysteresis [13].

So, complete understanding of properties of materials based on molybdenum disulphide requires additional studies. In present paper we provide the experimental data on electrical and magnetic properties obtained for the synthesized samples of different composition in system Fe_xMoS_2 (at $x = 0.1$, 0.2, 0.3).

2. Experiment

Such materials were synthesized by method of solid-state reactions in vacuum in vacuum-sealed quartz tubes. Source materials are carbonyl iron reduced in a stream of hydrogen, molybdenum grade M0 and elemental sulfur of ultra high purity (UHP). For finished products synthesis a two-stage procedure is used, when initially the input molybdenum disulphide is synthesized, and at second stage

MoS$_2$ is mixed with required amount of iron. From our opinion, this allowed to avoid direct interaction between free sulfur and iron metal, and formation of binary sulfide compounds of various metals which is enabled when samples are synthesized from initial elements. The primary and next homogenizing annealings after crushing and pressing of products were performed at $T = 750°\mathrm{C}$ for at least 100 h. X-ray certification of the original matrix MoSe$_2$ and intercalated samples Fe$_x$MoS$_2$ was performed at diffractometer Bruker D8 Advance in CuKα-radiation. It was confirmed that this procedure and used temperature-time mode ensured structure formation of studied compounds, corresponding to the modification 2H-MoS$_2$ (Figure 1, considering [14]).

The lattice cell was described under framework of the hexagonal structure (SG: P6$_3$/mmc.) with parameters $a = b = (3.159 \pm 0.005)$ Å and $c = (12.38 \pm 0.01)$ Å. It was stated earlier during structural studies, that for lamellar materials with anisotropic structure the size of regions of coherent scattering in different directions can differ significantly, resulting in anisotropic broadening of lines on the diffraction pattern and increases errors during the diffraction patterns processing [15]. Such diffraction patterns were obtained also for iron-containing samples. The intercalation of iron in MoS$_2$ resulted in change in the intensity of some reflexes, and changes of parameters a and c are not beyond the said errors.

Due to the fact that molybdenum disulfide and intercalated samples with low iron content had rather high electrical resistance values, measurements of the electrical properties of the synthesized samples were carried out using the two-probe method [16]. The conductive silver-containing paste was used to ensure reliable current and measuring contacts. The ohmic nature of contacts during measurements by this method was checked using current-voltage curves (CVCs). So, Figure 2 shows CVC for sample Fe$_{0.1}$MoS$_2$ with highest electrical resistance at two temperatures, having linear nature, and thus demonstrating absence of nonlinear effects at interface metal (contact)$-$semiconductor (sample). The magnetic susceptibility χ was studied by Faraday method in temperature range 80$-$300 K with automatic compensation of mechanical force acting on the sample in inhomogeneous magnetic field, and its transformation into the electric signal.

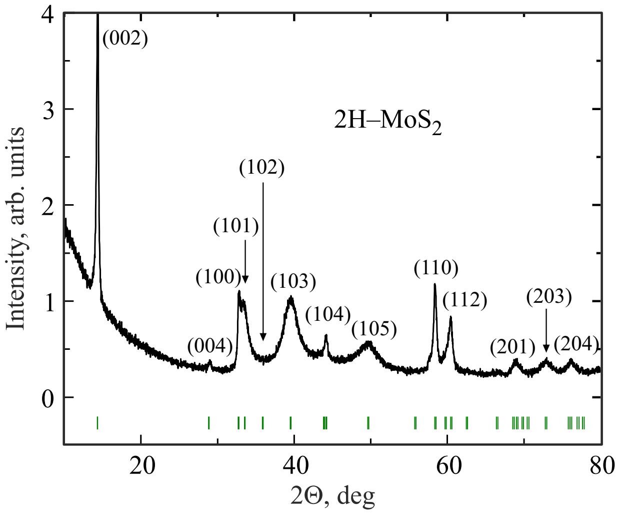

Figure 1. Diffraction pattern of original compound MoS$_2$. Arrows indicate position of Bragg reflections for hexagonal modification 2H-MoS$_2$ in accordance with International Data Base [14].

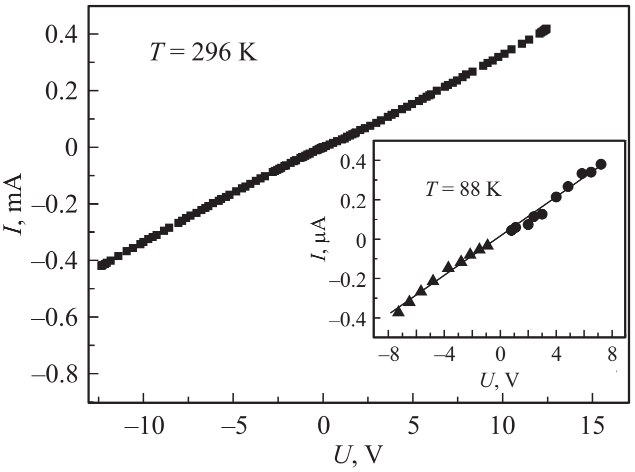

Figure 2. Current-voltage curves of Fe$_{0.1}$MoS$_2$ at two temperatures.

3. Results

The temperature dependences of the electrical resistance ρ for the synthesized samples Fe$_x$MoS$_2$ are shown in Figure 3. All shown dependences demonstrate activation nature of conductivity. Value of the electrical resistance significantly decreases with iron content increasing in samples. Here the logarithmic dependences of ρ on reciprocal temperature are also shown. For samples with $x = 0.2$ and 0.3 these dependences are shown by straight lines, and for Fe$_{0.1}$MoS$_2$ significant deviations from linearity are observed.

Considering possible mechanisms of charge transfer, we can not exclude that in highresistance state this process can be implemented as per hoping mechanism also. Possible presence in iron-containing samples of Fe^{2+} and Fe^{3+} ions does not exclude such assumption. In this case the charge transfer can occur over localized states in accordance with scheme

$$\mathrm{Fe}^{3+} + \mathrm{e}^- \leftrightarrow \mathrm{Fe}^{2+}. \quad (1)$$

To check such assumption a model of Mott hopping conductivity [17], which was previously used to analyze the conductivity mechanism in the intercalated compounds Cu$_x$HfSe$_2$ upon presence of copper ions with different valences [18]. The comparative data presented in Figure 4 for Fe$_{0.1}$MoS$_2$ in different coordinates using this model,

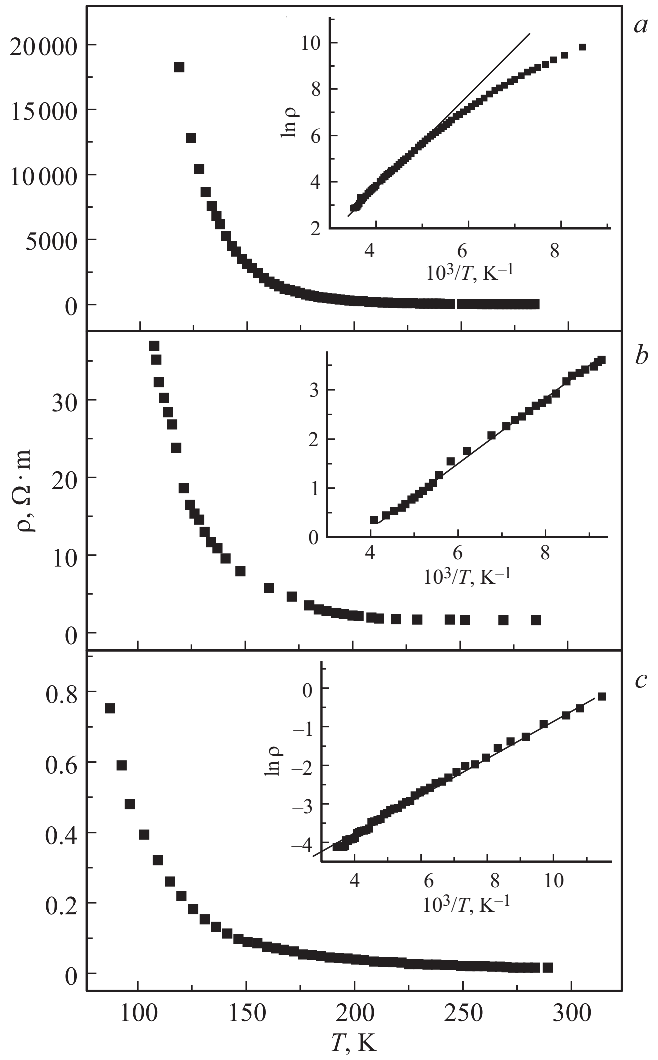

Figure 3. Temperature dependences of electrical resistance of intercalated compounds Fe_xMoS_2: *a*) $x = 0.1$, *b*) $x = 0.2$, *c*) $x = 0.3$. In inserts — appropriate logarithmic dependences of the electrical resistance on reciprocal temperature.

do not exclude such possibility. Significant increase in conductivity of samples with $x = 0.2$ and 0.3, and linear nature of dependences $\ln\rho(T^{-1})$ can be associated with the transition to impurity zone mechanism with increase in the content of intercalated atoms.

Results obtained during magnetic susceptibility χ measurements are shown in Figure 5. The magnetic susceptibility of molybdenum disulphide being matrix for next intercalation, at $T > 100\,\mathrm{K}$ has negative sign, although the temperature dependence χ is similar to same for paramagnetic state. The paramagnetic component of susceptibility of MoS_2 was determined during next data processing, this ensured evaluation of effective magnetic moment. For iron-containing samples the dependences $\chi(T)$ have different nature. So, for sample $Fe_{0.1}MoS_2$ the dependence $\chi(T)$ in the full studied temperature range has monotonic nature, and for samples with $x = 0.2$ and 0.3 these dependences have maximum at temperature $T_k = (125 \pm 5)\,\mathrm{K}$, this is close to values previously obtained for compound $FeMo_2S_4$ [12]. This maximum may indicate the existence of antiferromagnetic interactions between iron ions, and the indicated temperature may correspond to the Neel temperature.

Probably, in compound $Fe_{0.1}MoS_2$, due to lower concentration of iron atoms, the exchange interaction is more weaker, and transition into the antiferromagnetic state can be formed at lower temperatures.

Approximation of temperature dependences for each composition in region $T > T_k$ was performed according to Curie–Weiss law:

$$\chi(T) = \chi_0 + C(T - \Theta_p)^{-1}, \tag{2}$$

this ensured evaluation of temperature-independent contribution χ_0, Curie–Weiss constant C_1 and paramagnetic

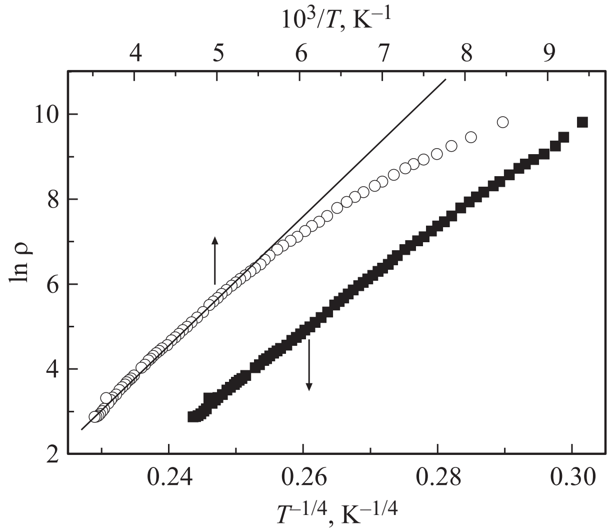

Figure 4. Dependences of logarithm of electrical resistance of $Fe_{0.1}MoS_2$ on reciprocal temperature with different degree dependence.

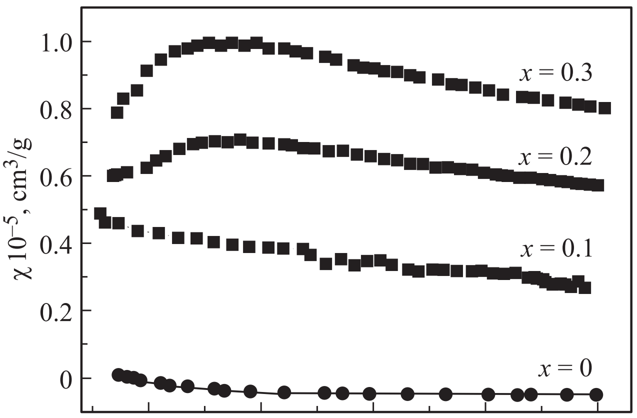

Figure 5. Temperature dependences of magnetic susceptibility of intercalated compounds Fe_xMoS_2.

Values of temperature independent contribution χ_0, paramagnetic Curie temperatures Θ_{p1} and Θ_{p2}, Curie–Weiss constants C_1 and C_2, effective magnetic moments calculated for formula unit μ_{eff}/f.u. and iron ion μ_{eff}/Fe for compounds Fe$_x$MoS$_2$

Compound	$10^{-6}\chi_0$, cm^3/g	Θ_{p1}, K	Θ_{p2}, K	C_1, 10^{-3} g/(K·cm^3)	C_2, 10^{-3} g/(K·cm^3)	μ_{eff}/f.u., μ_B	μ_{eff}/Fe, μ_B
MoS$_2$	−0.6	50	38	0.019	0.0184	0.16	–
Fe$_{0.1}$MoS$_2$	0.74	−144	−146	0.93	0.93	1.11	3.5
Fe$_{0.2}$MoS$_2$	1.6	−295	−300	2.46	2.44	1.83	4.1
Fe$_{0.3}$MoS$_2$	1.3	−366	−350	4.44	4.46	2.5	4.5

Curie temperature Θ_{p1}. Consideration of obtained values χ_0 made it possible to determine from measured values of susceptibility the Curie–Weiss contribution — second term in equation (2). Figure 6 demonstrates the linear nature of the temperature dependences of value $(\chi - \chi_0)^{-1}$ on temperature in region $T > T_k$. Such presentation also ensures determination of value of Curie–Weiss constant C_2 and of paramagnetic Curie Θ_{p2} temperature, thus checking authenticity of the made approximation. The results presented in the Table demonstrate good agreement between the two processing methods, and thus confirm the correctness of the approximation in accordance with (2).

The obtained data show that values Θ_p for all compositions have negative sign and increase by absolute value with increase in iron content in samples, this also characterizes the possibility (at $x = 0.1$) or presence (at $x = 0.2$ and 0.3) of antiferromagnetic order in these compounds. Table also shows values of effective magnetic moments calculated based on values of Curie–Weiss constants which show rise upon increase in iron content in samples. Anyway, values μ_{eff}/Fe remain lower than for high spin state of isolated Fe^{2+} ions (4.9μ_B) and Fe^{3+} (5.9μ_B).

Additional confirmation of presence of exchange interactions of antiferromagnetic type in Fe$_x$MoS$_2$ can be nature of temperature dependences of effective magnetic moments (Figure 7), which values increase upon temperature increasing. However, as can be seen, their values do not reach constant value in the temperature range studied, probably tending to the values indicated in the Table, but at higher temperatures.

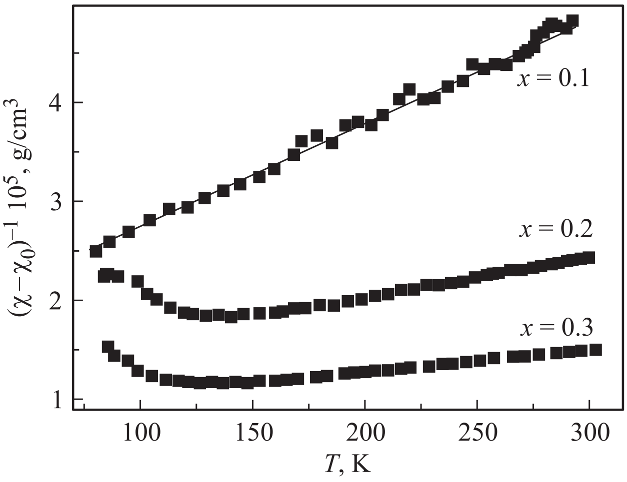

Figure 6. Temperature dependences of reciprocal Curie–Weiss contribution into magnetic susceptibility Fe$_x$MoS$_2$.

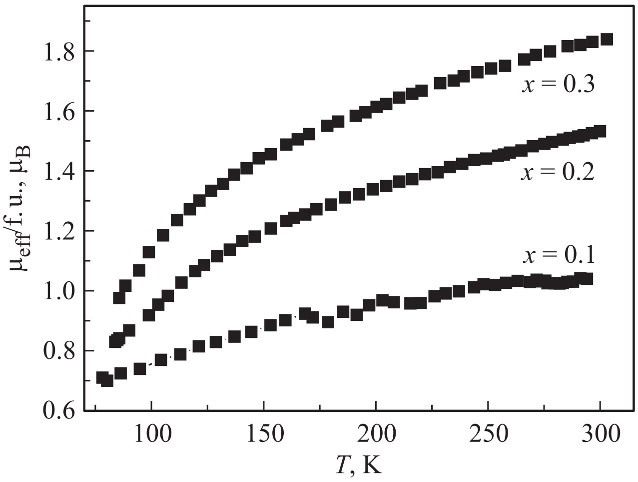

Figure 7. Temperature dependences of effective magnetic moments, determined per formula unit of compounds Fe$_x$MoS$_2$.

4. Conclusion

The temperature-time modes developed during the study for the synthesis of molybdenum disulphide and intercalated iron-containing samples made it possible to obtain compounds in the hexagonal modification corresponding to 2H-MoS$_2$. Study of the effect of iron atoms intercalation on the electrical properties of the compounds Fe$_x$MoS$_2$, made in the present paper, shows that the temperature dependences of the electrical resistance of the intercalated materials have activation nature. The activation nature of charge carriers is discussed under zone (with admixtures participation) and hopping mechanism associated with possible presence of iron ions with different valency.

As result the study of magnetic characteristics shows that magnetic state of molybdenum disulphide is formed in combination with diamagnetic and paramagnetic contributions. Determination of the paramagnetic contribution ensured evaluation of the effective magnetic moment of formula unit MoS$_2$ by 0.16μ_B. In intercalated compounds the exchange interactions of antiferromagnetic type prevail, which in $Fe_{0.2}MoS_2$ and $Fe_{0.3}MoS_2$ lead to setting of the antiferromagnetic state below $T = 125\,K$. It is expected that in compound with lower iron content such state can be formed at $T < 80\,K$. Negative values of paramagnetic Curie temperatures and the nature of the temperature dependences of effective magnetic moments also confirm the possibility of antiferromagnetic ordering in intercalated compounds Fe_xMoS_2.

Acknowledgments

We would like to express our gratitude to N.V. Selezneva for her assistance in radiographic qualification of the test objects.

Funding

This study was supported financially by the Ministry of Science and Higher Education of the Russian Federation (State Assignment No. FEUZ-2023-0017).

Conflict of interest

The author declares that she has no conflict of interest.

References

[1] L.A. Chernozatonskii, A.A. Artyukh. Phys. — Usp. **61**, *1*, 2 (2018).

[2] I.V. Antonova. Semiconductors **50**, *1*, 66 (2016).

[3] Y. Zhang, Y. Yao, M.G. Sendeku, L. Yin, X. Zhan, F. Wang, J. He. Adv. Mater. **31**, *41*, E 1901694 (2019). https://doi.org/10.1002/adma.201901694

[4] M. Inoue, H.P. Hughes, A.D. Yoffe. Adv. Phys. **38**, *5*, 565 (1989).

[5] N.V. Baranov, V.G. Pleshchev, A.N. Titov, V.I. Maksimov, N.V. Selezneva, E.M. Sherokalova. Nanotekhnika *3*, 15 (2008). (in Russian).

[6] V.G. Pleshchev, N.V. Mel'nikova, N.V. Selezneva. Phys. Solid State **60**, *7*, 1287 (2018).

[7] E.M. Sherokalova, N.V. Selezneva, V.G. Pleshchev. Phys. Solid State **64**, *4*, 434 (2022).

[8] V.G. Pleshchev. Phys. Solid State **65**, *8*, 1300 (2023).

[9] E.P. Domashevskaya, D.L. Goloshchapov, H.I.D. Al Khailani, E.V. Rudnev, M.V. Grechkina, S.V. Ryabtsev. Semiconductors **53**, *7*, 923 (2019).

[10] E.S. Kadantsev, P. Hawrylak. Solid State Commun. **152**, *10*, 909 (2012). https://doi.org/10.1016/j.ssc.2012.02.005

[11] P.B. James, M.T. Lavik. Acta Cryst. **16**, *11*, 1183 (1963).

[12] P. Vaquero, M.L. Kosidowski, A.V. Powell. Chem. Mater. **14**, *3*, 1201 (2002). https://doi.org/10.1021/cm010720k

[13] S. Fu, K. Kang, K. Shayan, A. Yoshimura, S. Dadras, X. Wang, L. Zhang, S. Chen, N. Liu, A. Jindal, X. Li, A.N. Pasupathy, A.N. Vamivakas, V. Meunier, S. Strauf, E.-H. Yang. Nature Commun. **11**, *1*, 2034 (2020). https://doi.org/10.1038/s41467-020-15877-7

[14] International Centre for Difraction Data-ICDD-2012 [Powder Difraction Database — PDF-2]. https://www.icdd.com

[15] P. Scardi, M. Leoni. Acta Cryst. A **57**, *5*, 604 (2001). https://doi.org/10.1107/S0108767301008881

[16] L.P. Pavlov. Metody izmereniya parametrov poluprovodnikovykh materialov. Vyssh. shk., M. (1987). 239 s. (in Russian).

[17] N.F. Mott, E.A. Davis. Electronic Processes in Non-Crystalline Materials. Clarendon Press, Oxford (1971).

[18] V.G. Pleshchev, N.V. Baranov, N.V. Melnikova, N.V. Selezneva. Phys. Solid State **54**, *7*, 1348 (2012).

Translated by I.Mazurov