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Magnitic status of molibden disulfide and intercalated compounds in the Cr-MoS$_2$ system

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In the system of synthesized phases with quasi-dimensional structure $\mathrm{Cr}_x\mathrm{MoS}_2$ at $0 \le x \le 0.5$ the magnetic properties of both initial molybdenum disulfide and intercalated compounds on its basis have been studied. For molybdenum disulfide the value of effective magnetic moment and paramagnetic Curie temperature with positive value were determined. The possibility of realization of magnetically ordered states of different type in compounds with different content of chromium atoms based on the analysis of temperature dependences of magnetic susceptibility, the sign of paramagnetic Curie temperature and the difference of temperature dependences of effective magnetic moments is shown.

Keywords: molybdenum disulfide, chromium, intercalation, magnetic susceptibility, effective magnetic moment.

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1. Introduction

Systems with crystal structure of reduced dimensionality have attracted increasing interest of researchers in recent years [1–4]. The layered structure of materials such as dichalcogenides of groups 4, 5, 6 of the Periodic Table with the general formula TX_2 is formed due to differences in the nature of chemical bonding within the three-layer blocks $X-T-X$ and between individual blocks and determines the strong anisotropy of properties along and across the layers. These materials, depending on the position of the metal in the Periodic Table, can have different structural modifications (polytypes), differing in the position of atoms and the number of layers TX_2 in the lattice cell. In particular, molybdenum disulfide can exist in an unstable $1T$-modification similar to titanium or hafnium dichalcogenides, of thermodynamically equilibrium $2H$-modifications with hexagonal structure (SG: $P6_3/mmc$) and $3R$-modifications with rhombohedral structure (SG: $P3m1$).

For example, the lattice cell of $2H$-phase contains two layers of MoS$_2$ with trigonal-prismatic environment of molybdenum atoms [2,4,5] in contrast to $1T$-MoS$_2$ with octahedral coordination of metal atoms. $2H$-MoS$_2$ is a semiconductor in terms of its electrical properties due to the peculiarity of the electronic structure with a band gap width of more than 1 eV [6,7]. The literature indicates that the physical properties of this material depend on the number of layers of MoS$_2$. Thus, the bulk samples of MoS$_2$ intercalated with iron exhibited an antiferromagnetic state [8], while the synthesized iron-doped monolayers exhibited ferromagnetic properties up to room temperature [9,10].

Weak bonding between the layers and a significant distance between them, comparable to the size of the blocks themselves allows the process of introduction (intercalation) between the blocks of MoS$_2$ atoms of other elements, including elements with unfilled $3d$-shell. The nature of the change in the properties of the intercalated compounds depends not only on the variety of the introduced $3d$-atoms, but also on the type of the initial matrix MX_2 [1,2]. Previously, study of chromium intercalated titanium diselenides $\mathrm{Cr}_x\mathrm{TiSe}_2$ showed that samples with chromium content $x = 0.5$ exhibited antiferromagnetic ordering below the Neel temperature of 38 K [11], while $\mathrm{Cr}_{0.5}\mathrm{TiTe}_2$ compounds exhibited a ferromagnetic-type state at temperatures below 78 K [12]. No long-range magnetic order was detected in $\mathrm{Cr}_x\mathrm{VSe}_2$ samples up to chromium concentration $x = 0.33$, but a transition to the spin-steel state takes place at low temperatures [13]. The system of $\mathrm{Fe}_x\mathrm{TiSe}_2$ [14] exhibited antiferromagnetic properties, while the field dependences of the magnetization in $\mathrm{Fe}_x\mathrm{HfS}_2$ were characterized by hysteresis, indicating the presence of a ferromagnetic state [15]. The study of the system $\mathrm{Cr}_x\mathrm{MoSe}_2$ found that $\mathrm{Cr}_x\mathrm{MoSe}_2$ compounds are in the paramagnetic state in the temperature region of 150–350 K, and the exchange interactions increase at lower temperatures leading to the formation of ferromagnetic-type magnetic order with characteristic features of magnetic and thermomagnetic hysteresis [16].

Considering the above-mentioned significant dependence of the magnetic properties of intercalated phases on the nature of the initial matrix, the present work presents the results of studying the magnetic characteristics of molybdenum disulfide, as well as intercalated chromium-containing compounds based on it $\mathrm{Cr}_x\mathrm{MoS}_2$ ($0 \le x \le 0.5$).

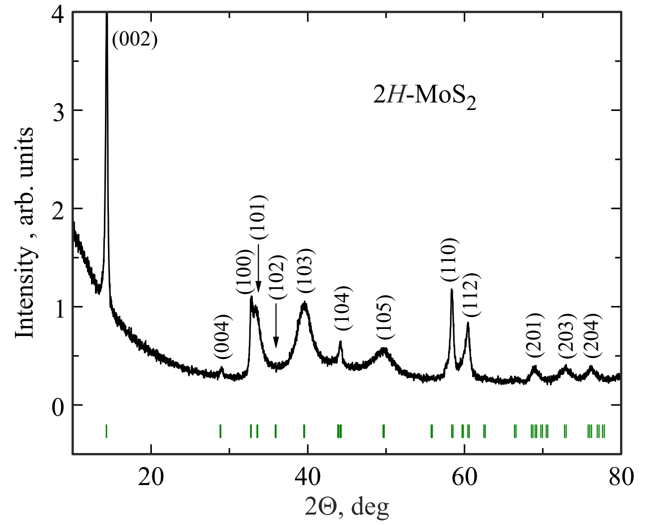

Figure 1. Diffraction pattern of original compound MoS_2. The lower dashes indicate the positions of the Bragg reflections for the hexagonal modification of 2H-MoS_2 according to the International Database (Card Number 00-037-1492) [17].

2. Experiment

These materials were synthesized by solid-phase reactions in vacuum-quenched quartz ampoules followed by multiple homogenization. Electrolytic chromium, M0 grade molybdenum and elemental sulfur of special purity were the starting materials. The final products were synthesized by using a two-step procedure, described in detail in a number of papers [12–16], in which the initial molybdenum disulfide was synthesized initially, and in the second MoS_2 was mixed with the required amount of chromium. Repeated grinding and pressing of the intermediates ensured the homogeneity of the final products, which was confirmed by X-ray examination of their various fragments. It was confirmed by X-ray analysis that the two-step procedure and the temperature-time mode used ensured the formation of the structure of the studied compounds corresponding to the modification 2H-MoS_2 (Figure 1). The lattice cell has been described within a hexagonal structure (SG: $P6_3/mmc$) with parameters $a = b = (3.159 \pm 0.005)$ Å and $c = (12.38 \pm 0.01)$ Å whose values are in the range of values obtained for MoS_2 in various papers [3,5,18].

The magnetic susceptibility (χ) of polycrystalline samples of Cr_xMoS_2 was studied by Faraday method in the temperature range of 80−300 K on scales with automatic compensation of the mechanical force acting on the sample in a non-uniform magnetic field and its conversion into an electrical signal. Powdered samples of small size in a quartz container, were suspended on a quartz thread to one of the arms of a scale so as to be in the region of the magnetic field where the product $H \cdot dH/dz$ maintained its value with an error of not more than 10 %.

3. Results

Figure 2 shows the data obtained from the study of magnetic properties of molybdenum disulfide. The magnetic susceptibility in the studied temperature region has a negative sign, which is typical for the majority of semiconductor compounds of this class, but the character of its temperature dependence more resembles such dependence for a paramagnetic (Figure 2, a). A similar dependence with negative susceptibility values was given in a previously published paper in Ref. [19] for MoS_2 single crystals. The analysis of this dependence and subsequently similar dependences of chromium-containing compounds was carried out in accordance with the generalized Curie−Weiss law:

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

where χ_0 is the temperature-independent summand, C is the Curie constant−Weiss; Θ_p is the paramagnetic Curie

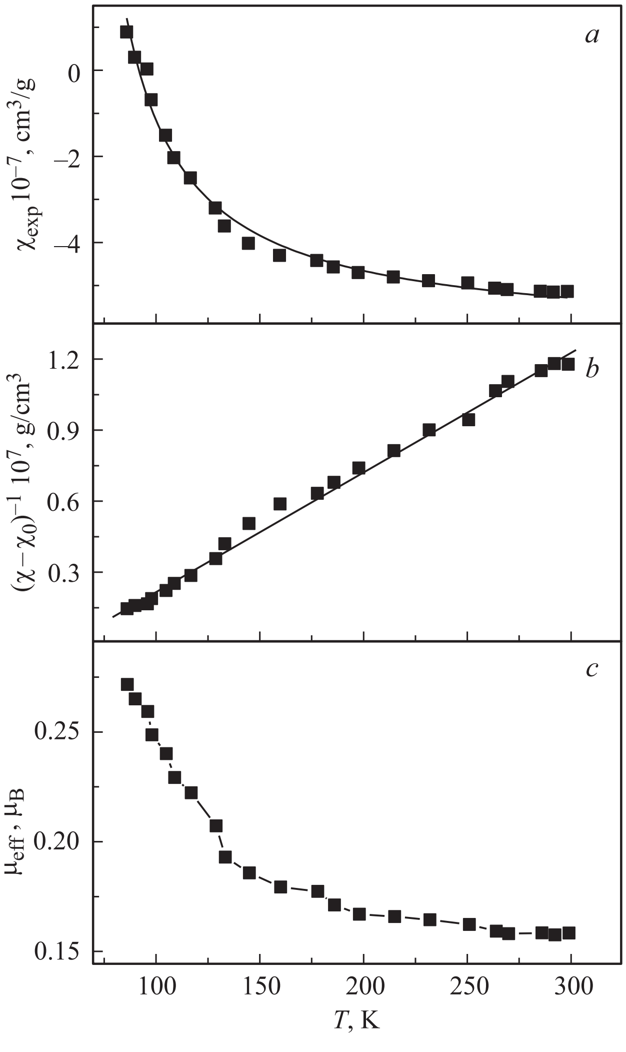

Figure 2. Temperature dependences: (a) of the measured magnetic susceptibility χ_{exp}, (squares — experiment; line — approximation result in accordance with expression (1); (b) inverse Curie−Weiss contribution $(\chi - \chi_0)^{-1}$; (c) effective magnetic moment of MoS_2.

temperature, the sign and magnitude of which reflect the average value of the algebraic sum of exchange interactions of different sign between localized moments. It was assumed in the first approximation that the value χ_0, which includes the diamagnetic contribution, is independent of temperature. The result of this approximation determined the parameters included in (1), namely, the values of $\chi_0 = -5.8 \cdot 10^{-7}\,\mathrm{cm^3/g}$, the Curie–Weiss constant C, and the paramagnetic Curie temperature $\Theta_p = 48\,\mathrm{K}$. The value of C was further used to calculate the effective magnetic moment according to the well-known formula

$$\mu_{\text{eff}} = (3k \cdot C/N \cdot \mu_{\text{B}}^2)^{1/2}, \tag{2}$$

where k is the Boltzmann constant, N is the number of MoS$_2$ molecules in the sample mass unit, μ_{B} is the Bohr magneton.

When the obtained value of χ_0 was taken into account, the dependence of the Curie–Weiss contribution was obtained, which had a positive value and actually repeated the appearance of the original dependence $\chi_{\text{exp}}(T)$. The approximation of this dependence according to (1) gave the same results regarding C and Θ_p as above. The inverse Curie–Weiss contribution $(\chi - \chi_0)^{-1}$ on Figure 2, *b* shows a good linear temperature dependence, the processing of which, in turn, further confirmed the validity of the parameters obtained from the approximation results.

The rather high positive value of the paramagnetic Curie temperature, which indicates the possibility of realization of ferromagnetic-type interactions in MoS$_2$. This possibility is also indicated by the temperature dependence of the effective magnetic moment (Figure 2, *c*). As can be seen, its value tends to a value with increasing temperature, which coincides with the calculated value of the effective magnetic moment $0.16\mu_{\text{B}}$ obtained using expression (2). A similar kind of dependence $\chi(T)$ with negative susceptibility values was obtained by other authors in Ref. [10], where it was reported that the total magnetic susceptibility of MoS$_2$ included both diamagnetic and ferromagnetic parts, and after the separation of the diamagnetic contribution, the measured field dependences of the magnetization had a nonlinear appearance similar to the ferromagnetic magnetization curves. In the temperature region studied by us, we can only assert the presence of temperature-dependent paramagnetism, where the corresponding states, according to the authors in Refs. [10,19] may be related to broken bonds at grain boundaries, vacancies, and localized boundary states. The properties of different polymorphic modifications of MoS$_2$ can differ significantly from each other due to the lattice configuration and distribution of electron orbitals. In the case of 2*H*-MoS$_2$ 4*d* the molybdenum orbitals split into two degenerate orbitals d_{xy} and d_{xz}, two degenerate orbitals $d_{x^2-y^2}$ and d_{xy} and orbital d_{z^2} [19,20]. According to crystal field theory, the energy level of the orbital d_{z^2} is located well below the orbitals $d_{x^2-y^2}$ and d_{xy}. Since two electrons stay in the *d*-orbitals, in Mo^{4+} the filling of d_{z^2}-orbitals in the 2*H*-MoS$_2$ phase becomes more preferable [19,20]. For this reason the relatively small value of $\mu_{\text{eff}} = 0.16\mu_{\text{B}}$ in case of the pairwise filling of d_{z^2}-orbital and the observed paramagnetic behavior of MoS$_2$ should not be attributed to uncompensated spin moments. Their origin is probably related to polarization effects in the magnetic field, to broken bonds at grain boundaries [10,20], and (or) to the presence of structural defects that distort the electronic structure. In comparison, the ion Nb^{4+} of niobium diselenide has one unpaired electron in 4*d*-shell and $\mu_{\text{eff}} = 0.56\mu_{\text{B}}$ in 2*H*-phase, where the distribution of 4*d*-orbitals is similar to MoS$_2$ [21].

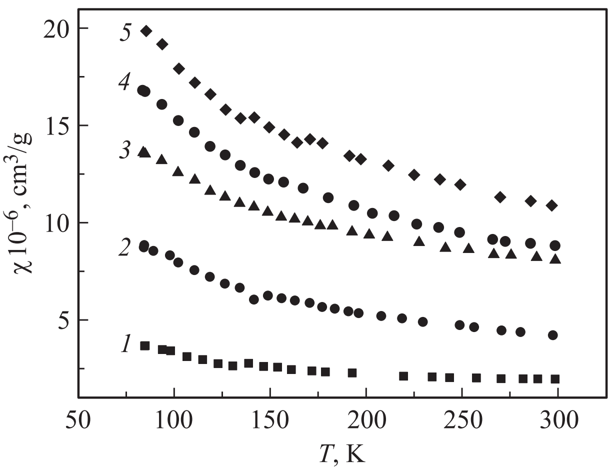

Figure 3. Temperature dependences of magnetic susceptibility of intercalated compounds Cr$_x$MoS$_2$: $x = 0.1$ (*1*); $x = 0.2$ (*2*); $x = 0.25$ (*3*); $x = 0.33$ (*4*); $x = 0.5$ (*5*).

Figure 3 shows the temperature dependences of the magnetic susceptibility of the intercalated compounds Cr$_x$MoS$_2$. As can be seen, the magnitude of the magnetic susceptibility decreases nonlinearly with increasing temperature for each compound composition and monotonically increases with increasing chromium content, but the inverse of χ for all compositions in the studied temperature region was nonlinear.

The relationships $\chi(T)$ in Figure 3 were also processed according to expression (1), resulting in the values of χ_0, C, and Θ_p for samples of different compositions. It was determined that the value of χ_0 for chromium-containing compounds has a positive value, accounting for an appreciable fraction of the total susceptibility, and increases with increasing chromium content in the samples (Figure 4). The concentration dependence of paramagnetic Curie temperature values at $0 \le x \le 0.5$ is also presented there. Taking into account the values χ_0 obtained as a result of the approximation allowed us to define the Curie–Weiss contribution to the magnetic susceptibility, which is confirmed by the data presented in Figure 5 that shows the dependences of $(\chi - \chi_0)^{-1}$ on temperature. The values of C and Θ_p were also determined from the data presented in Figure 5, which were almost identical to those determined from the results of the approximation of the temperature dependences of magnetic susceptibility in Figure 3. This confirms the sufficient reliability and validity of the analysis performed. The values of the effective magnetic moments in the intercalated compounds were determined per formula unit of each compound and per chromium ion. The collected data are presented in Figure 6.

As determined by processing the experimental data, the paramagnetic Curie temperature value for the compound $Cr_{0.1}MoS_2$ had a positive value $\Theta_p = 21\,K$ as that of the original molybdenum disulfide. The values of Θ_p became negative with increasing chromium content, which is reflected in Figure 4. Since this value reflects the nature of the prevailing exchange interactions, it is to be assumed that their ferromagnetic character at low chromium contents changes to antiferromagnetic character with increasing chromium concentration. The changing nature of interactions in the magnetic subsystem is also indicated by the different type of temperature dependences of the effective magnetic moment localized on chromium ions at different concentrations (Figure 7). It is likely that the $3d$-electrons of chromium participate in intramolecular interactions with $4d$-electrons of molybdenum, similar to that indicated for MoS_2 monolayers doped with iron [10], which leads to the predominance of antiferromagnetic-type interactions as the chromium concentration increases.

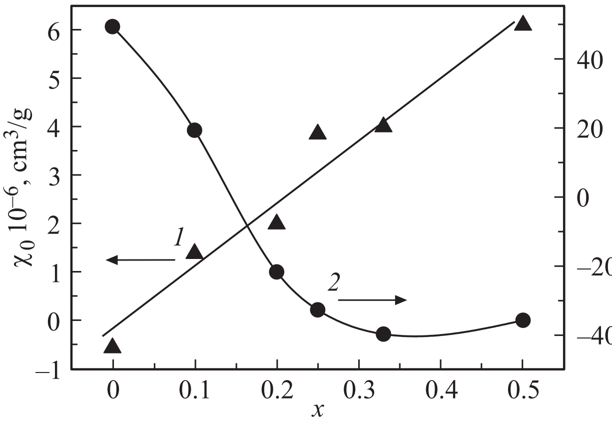

Figure 4. Concentration dependences of χ_0 (*1*) and paramagnetic Curie temperature Θ_p (*2*) of compounds Cr_xMoS_2.

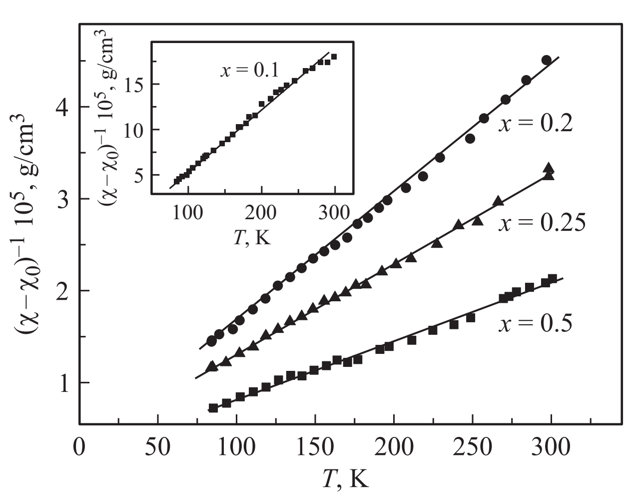

Figure 5. Temperature dependences of the inverse Curie-Weiss contribution $(\chi-\chi_0)^{-1}$ of Cr_xMoS_2 compounds.

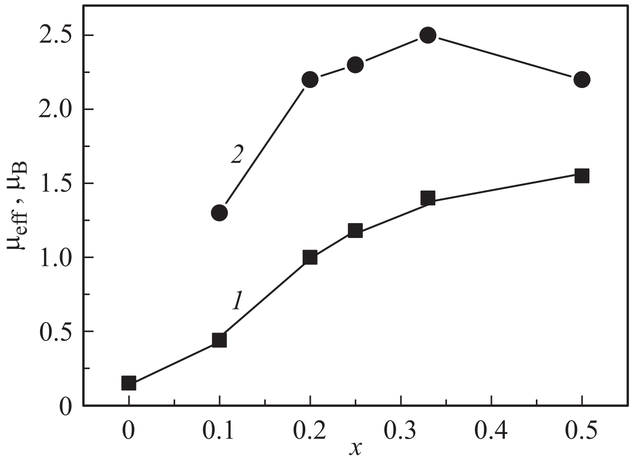

Figure 6. Concentration dependences of effective magnetic moments per formula unit Cr_xMoS_2 (*1*) and per chromium ion (*2*).

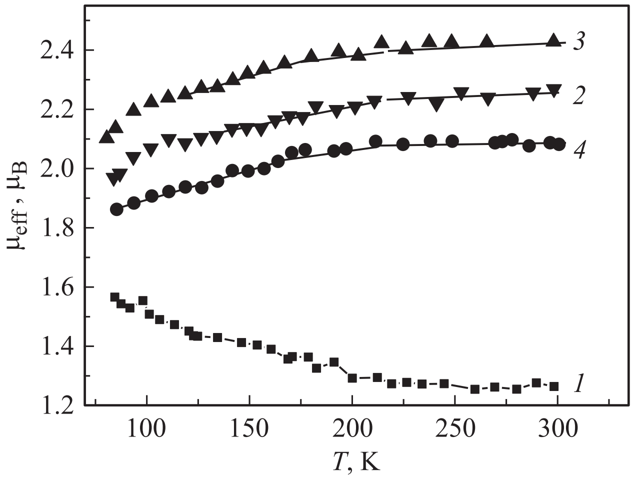

Figure 7. Temperature dependences of effective magnetic moments per chromium ion in compounds Cr_xMoS_2: $x = 0.1$ (*1*); $x = 0.25$ (*2*); $x = 0.33$ (*3*); $x = 0.5$ (*4*).

4. Conclusion

This work pays considerable attention to the analysis of the magnetic state of molybdenum disulfide, which serves as a matrix for the intercalation of chromium atoms in Cr_xMoS_2. The magnetic susceptibility of MoS_2 is found to include diamagnetic and Curie–Weiss contributions. The paramagnetic Curie temperature is shown to have a positive sign, confirming the few available literature data about the possibility of ferromagnetism in MoS_2. The value of the effective magnetic moment MoS_2 was determined for the first time in the study, both on the basis of data obtained by approximating the experimental dependences of magnetic susceptibility and by studying the temperature dependences of effective magnetic moments for compounds of different compositions. Based on the data on the electronic structure and distribution of $4d$-electrons of molybdenum in the corresponding orbitals, it was concluded that the effective moment of MoS_2 determined in the present work is most likely not related to the parallel orientation of electron spins in the $4d^2$ configuration, but to the possibility of polarization in a magnetic field and distortions of the electronic structure associated with the presence of defects.

The positive value of paramagnetic Curie temperature was also maintained in $Cr_{0.1}MoS_2$ compound, and changed to negative with increasing chromium content. It is concluded that $3d$-electrons of chromium and $4d$-electrons of molybdenum are involved in the formation of antiferromagnetic-type exchange bonding, which increases with increasing concentration of intercalated atoms. The changing nature of the interaction in the magnetic subsystem of the intercalated phases was confirmed by different kinds of temperature dependences of effective magnetic moments for compounds of different composition.

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Conflict of interest

The author declares that he has no conflict of interest.

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