Evolution of magnetic properties upon separate and joint intercalation of hafnium diselenide by copper and chromium atoms

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An analysis of the nature of the change in magnetic properties in the $Cr-Cr-Cu-HfSe_2$ system as a result of separate and joint intercalation of hafnium diselenide by chromium and copper atoms is presented. It is shown that a paramagnetic state is formed in three-component systems, which is described by the Curie-Weiss law. In $Cu_xCr_{0.25}HfSe_2$ compounds, when approximating the temperature dependences of the magnetic susceptibility, the dependence of the effective magnetic moments in magnitude and the Curie paramagnetic temperature in magnitude and sign on the temperature range of approximation was noted. When this interval was shifted to higher temperatures, there was a monotonous decrease in the magnitude of the effective magnetic moments and a change in the sign of the paramagnetic Curie temperature from negative to positive. To describe this dependence, it is proposed to use alternative models for the formation of the magnetic state.

Keywords: hafnium diselenide, intercalation, magnetic susceptibility, effective magnetic moment.

1. Introduction

A very interesting combination of various properties is noted in the papers devoted to studies of layered transition metal dichalcogenides (LTMD) [1–3]. Attention is also drawn to the unique opportunity to modify the properties of the original LTMD compounds within a wide range by intercalating various elements in them, thereby creating an alternation of two-dimensional scale structural fragments.

Previously studied temperature and field dependences of magnetization and magnetic susceptibility (χ) of samples Cr_xTiSe_2 [4,5], Cr_xTiTe_2 ($x \leq 0.5$) [6,7] and Cr_xVSe_2 [8] showed that the value χ increases with an increase in the chromium content, its temperature dependences at $T > 100$ K correspond to the paramagnetic state. At lower temperatures in the compound $Cr_{0.5}TiSe_2$ [5], an antiferromagnetic state is formed with a Neel temperature $T_N = 38$ K, characterized by the effect of spin reorientation at a relatively low magnetic field strength. In the Cr_xTiTe_2 system, along with the formation of a spin glass state with critical temperatures $T_k = 8$ K ($x = 0.2$) and $T_k = 10$ K ($x = 0.25$) ferromagnetic states with Curie temperatures $T_c = 12$ K and $T_c = 78$ K at $x = 0.33$ and $x = 0.5$, respectively, were observed [6]. The dependences $M(H)$ at $T = 2$ K showed a pronounced magnetic hysteresis in these compounds. The hysteresis loops had a symmetrical shape with coercive force $H_c = 200$ Oe ($x = 0.33$) and $H_c = 700$ Oe ($x = 0.5$). No long-range magnetic order was detected in the Cr_xVSe_2 system, unlike other chromium-containing systems. This emphasizes the important role of LTMD nature in the formation of intercalated compounds physical properties.

The concentration dependences of the effective magnetic moments obtained by linear extrapolation of the dependences $\chi^{-1}(T)$ showed that in the system Cr_xTiSe_2 the effective magnetic moment on the chromium ion (μ_{eff}/Cr) decreases with the introduction of chromium up to up to the composition with $x = 0.25$, and then increases, nevertheless remaining below the value characteristic of the spin moment ($S = 3/2$) of the ion Cr^{3+} ($3.87\mu_B$). The reason for this behavior was associated with the partial delocalization $3d$ of chromium electrons and their possible participation in the formation of a covalent bond with $TiSe_2$ molecular orbitals. This was confirmed by a significant compression of the crystal lattice during the introduction of chromium in the system Cr_xTiSe_2 [4]. The temperature dependences of the electrical resistivity for these compositions were, as a rule, metallic in nature and could be represented as the sum of the electron-phonon contribution and the contribution from scattering on impurities.

Hafnium diselenide is a chemical and structural analog of titanium diselenide and belongs to the class of materials with a quasi-two-dimensional structure described in the framework of a trigonal syngony (space group $P\bar{3}m1$) [9,10]. The lattice cell contains one layer $Se-Hf-Se$, in which metal atoms are located in an octahedral environment of selenium atoms. The distance between the layers is greater than in $TiSe_2$ due to the increase in the lattice cell parameters in hafnium diselenide. As a result, the interaction between them should be weaker, which makes the two-dimensional nature of the $HfSe_2$ structure more pronounced. An important feature of the structure of LTMD compounds is the presence of vacancies between the matrix layers for intercalated atoms with octahedral and tetrahedral

surroundings by chalcogen atoms. As follows from the available data [10], the preference for their filling during intercalation is determined by the degree of covalence of bonds in the matrix itself and the electronic structure of the atoms (ions) embedded in the dichalcogenide.

The data obtained during studies of optical absorption and reflection showed that there is an energy gap $1.13-1.33$ eV between the valence band and the conduction band $HfSe_2$ [11–13]. As a result, hafnium diselenide has significantly greater electrical resistance compared to titanium diselenide and exhibits semiconductor properties, which is also characteristic of intercalated materials based on it. Electrical characteristics of hafnium diselenide samples intercalated with copper atoms were carried out in constant and alternating electric fields. They showed that the localization of charge carriers and the occurrence of hopping conductivity occurs during charge transfer due to the perturbation of the lattice potential in case of the disordered placement of copper ions between the layers of $Se-Hf-Se$ [14,15].

This paper presents the results of a study of the magnetic properties of compounds based on hafnium diselenide, separately intercalated with copper and chromium atoms, as well as compounds during joint intercalation using a series of phases $Cu_xCr_{0.25}HfSe_2$.

2. Experiment

Polycrystalline samples intercalated with copper (Cu_xHfSe_2, $x = 0.1$; 0.2), chromium ($Cr_{0.25}HfSe_2$) and samples with mixed intercalation $Cu_xCr_{0.25}HfSe_2$ ($x = 0.1$; 0.2) were obtained by standard step ampoule synthesis from titanium diselenide and corresponding elements of high purity at $T = 800°C$. The details of the synthesis are described in the previously published papers [4–7].

The magnetic moment of the samples (M) was measured using a SQUID magnetometer (MPMS) in the temperature range $2-350$ K and in the magnetic field $H = 10$ kOe. The temperature dependences of the electrical resistance of the samples were measured on direct current using a standard 4-contact method on a unit using an autonomous closed-loop cryostat CryoFree204.

3. Results

Temperature dependences of magnetic susceptibility ($\chi = M/H$) for various systems are shown in Figs. 1 and 2. Hafnium diselenide is a diamagnet by its magnetic properties, and when copper is introduced, negative values of magnetic susceptibility remain in the room temperature range.

An increase in the copper content in Cu_xHfSe_2 samples leads to an increase in magnetic susceptibility. At low temperatures, the paramagnetic component prevails, which may be associated with the presence of divalent copper ions
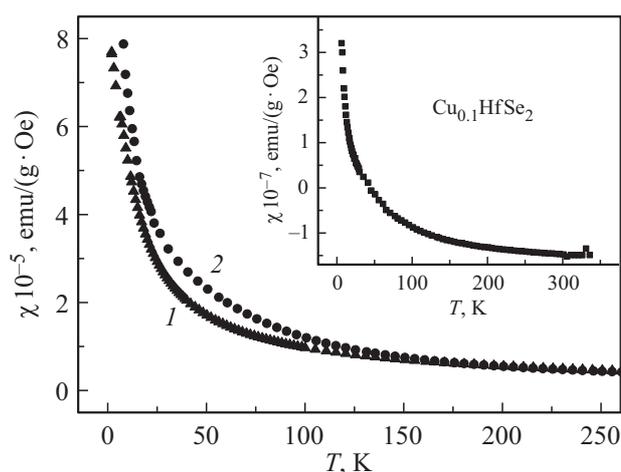
Figure 1. Temperature dependences of magnetic susceptibility of $Cu_{0.1}HfSe_2$ (in the insert), $Cr_{0.25}HfSe_2$ (*1*) and $Cu_{0.1}Cr_{0.25}HfSe_2$ (*2*).
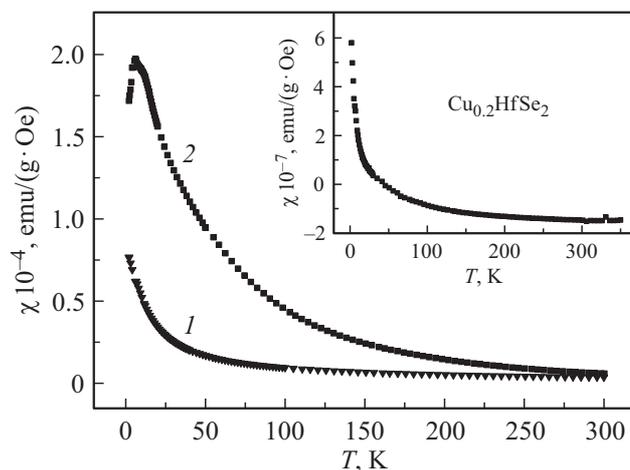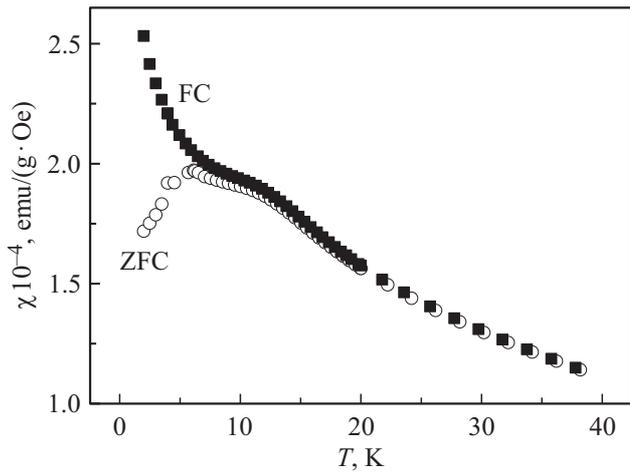

Figure 2. Temperature dependences of magnetic susceptibility of $Cu_{0.2}HfSe_2$ (in the insert), $Cr_{0.25}HfSe_2$ (*1*) and $Cu_{0.2}Cr_{0.25}HfSe_2$ (*2*).

in these compounds, in the 3*d*-shell of which one unpaired electron is preserved. In the approximation of localized states, the effective spin magnetic moment of such an ion is $1.73 \mu_B$.

The temperature dependence of the magnetic susceptibility $Cr_{0.25}HfSe_2$ has a monotonic character and corresponds to the paramagnetic state throughout the studied temperature range. The susceptibility values increase by about two orders of magnitude compared with Cu_xHfSe_2 samples. In addition, in the low temperature region, the dependence of the inverse susceptibility on temperature deviated from the linear dependence, indicating the existence of antiferromagnetic interactions, which is confirmed by the calculations presented below.

The additional introduction of copper atoms in $Cu_xCr_{0.25}HfSe_2$ samples led to a further increase in magnetic susceptibility, most noticeable in the low and
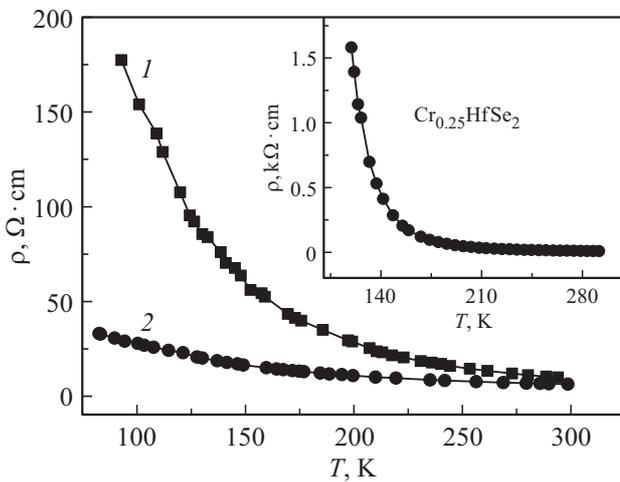
Figure 3. Low-temperature section of temperature dependence of magnetic susceptibility $Cu_{0.2}Cr_{0.25}HfSe_2$.

Figure 4. Temperature dependences of electrical resistivity $Cr_{0.25}HfSe_2$ (in the insert), $Cu_{0.1}Cr_{0.25}HfSe_2$ (*1*) and $Cu_{0.2}Cr_{0.25}HfSe_2$ (*2*).

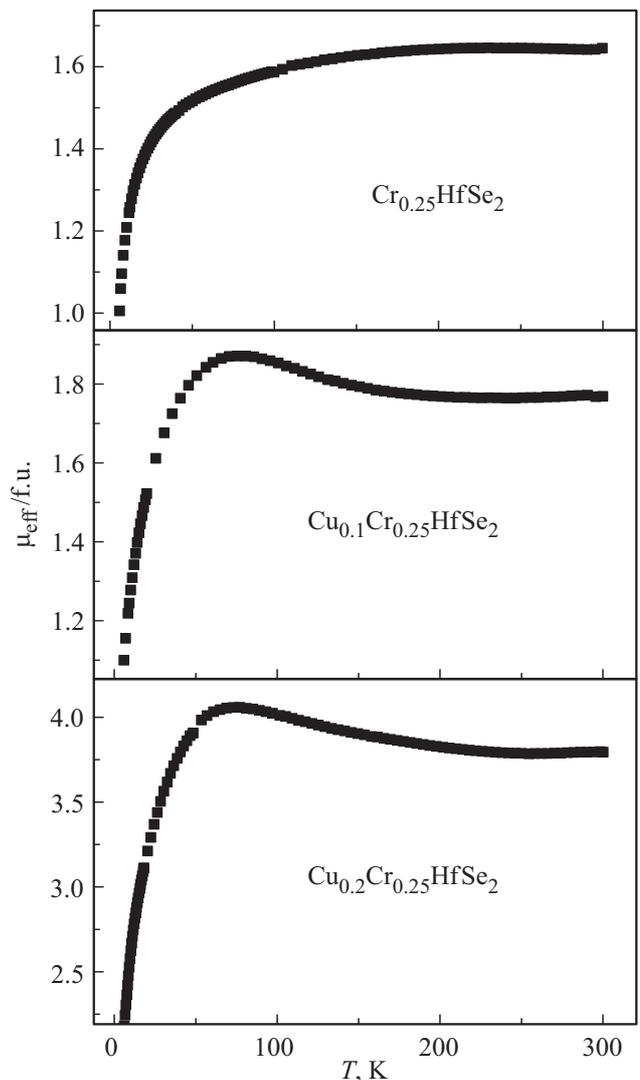medium temperature region. At low temperatures in $Cu_{0.2}Cr_{0.25}HfSe_2$, hysteresis was observed during magnetization measurements in ZFC and FC modes, indicating the formation of a spin glass phase with a critical temperature of about 7 K (Fig. 3).

A significant decrease of electrical resistance was also observed in addition to the noted impact of copper ions on the magnetic properties of compounds with mixed intercalation which may be associated with additional ionization of copper ions and an increase in the concentration of charge carriers (Fig. 4).

The approximation of the obtained temperature dependences of magnetic susceptibility in all cases was carried out on the basis of the generalized Curie−Weiss equation.

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

where χ_0 — a summand representing the sum of temperature-independent diamagnetic and paramagnetic

(Pauli) contributions, C — Curie−Weiss constant, Θ_p — paramagnetic Curie temperature, the magnitude and sign of which characterize the magnitude and nature of possible interactions in the subsystem of magnetic moments.

Dependencies $\chi(T)$ of compounds Cu_xHfSe_2 and $Cr_{0.25}HfSe_2$ in temperature ranges $5-330$ K and $100-330$ K are well described by the equation (1). At the same time, the different choice of the temperature range of approximation practically does not affect the parameters C and Θ_p, as shown in the table. A lower value of μ_{eff} calculated for the copper ion in $Cu_{0.2}HfSe_2$ may be associated with a lower concentration of divalent copper ions. Based on the values obtained, estimates were made of the possible number of such ions in relation to the actual copper content, which amounted to about 7% for $Cu_{0.1}HfSe_2$ and about 5% for $Cu_{0.2}HfSe_2$.

Since the magnetic susceptibility in samples with mixed intercalation is determined by various contributions (Cu and Cr), when processing experimental data in accor-

Figure 5. Temperature dependences of the effective magnetic moment for $Cr_{0.25}HfSe_2$ and $Cu_xCr_{0.25}HfSe_2$.

Values of the constant Curie−Weiss C, paramagnetic Curie temperature Θ_p, effective magnetic moment per formula unit μ_{eff}/f.u. and per copper or chromium ion μ_{eff}/ion, respectively, at different intervals approximations ΔT for samples in the system Cu−Cr−HfSe$_2$

Connection	ΔT, K	C, K · emu/g · Oe	Θ_p, K	μ_{eff}/f.u., μB	μ_{eff}/ion, μB
Cu$_{0.1}$HfSe$_2$	5−330	9.4e-6	−15	0.145	0.46
	100−330	8.9-6	−12	0.14	0.44
Cu$_{0.2}$HfSe$_2$	5−330	1.1e-5	−4	0.175	0.41
	100−330	9.3e-6	−1.4	0.16	0.38
Cr$_{0.25}$HfSe$_2$	10−300	1.02e-3	−12	1.67	3.34
	100−300	1.17e-3	−24	1.81	3.48
Cu$_{0.1}$Cr$_{0.25}$HfSe$_2$	20−240	1.91e-3	−23	2.33	
	25−300	1.73e-3	−19	2.21	
	2−300	1.25e-3	−11	2.15	
	50−300	1.16e-3	−4.6	1.96	
	70−300	1.07e-3	11	1.74	
	100−300	0.91e-3	22	1.61	
Cu$_{0.2}$Cr$_{0.25}$HfSe$_2$	15−240	11.2e-3	−38.7	5.7	
	24−240	10.4e-3	−35	5.48	
	25−300	9.13e-3	−28	5.14	
	50−300	6.21e-3	−3	4.23	
	70−300	5.29e-3	7	3.91	
	100−300	4.64e-3	17	3.66	

dance with (1), only the effective magnetic moments per compound molecule (formula unit — μ_{eff}/f.u.) could be determined. The results of calculations are presented in the table. In the case of non-interacting and localized magnetic moments, the value of μ_{eff}/f.u. is related to the effective magnetic moments of various ions by the ratio

$$(\mu_{\text{eff}}/\text{f.u.})^2 = 0.25 \cdot (\mu_{\text{eff}}/\text{Cr})^2 + x \cdot (\mu_{\text{eff}}/\text{Cu})^2, \quad (2)$$

where μ_{eff}/f.u. — the value obtained from the experiment, x — the coefficient corresponding to the copper content in the formula unit. Calculations to verify the feasibility of this ratio were performed under the condition that the moment of chromium ions (μ_{eff}/Cr) is equal to its value in the original compound Cr$_{0.25}$HfSe$_2$ (on average $3.4 \mu_B$), and for copper (μ_{eff}/Cu) in samples with different copper content $0.46 \mu_B$ and $0.4 \mu_B$ (see table).

Numerical estimates of the right side of the expression performed under these conditions (2) showed that for the Cu$_{0.1}$Cr$_{0.25}$HfSe$_2$ compound, this equality within the error of determination of μ_{eff} is fulfilled only when taking into account the results of the most high-temperature approximation interval. Under the same conditions, for Cu$_{0.2}$Cr$_{0.25}$HfSe$_2$, the sum of the terms in the right part turns out to be several times less than the experimental value $(\mu_{\text{eff}}/\text{f.u.})^2$. The analysis of the data given in the table

for phases with joint intercalation indicates the dependence of the parameter values in (1) on the choice of the approximation interval. It can be seen that, this applies to the values of C, and, consequently, μ_{eff} and the value of Θ_p. Curie−Weiss constant monotonously decreases when the approximation interval shifts to the region of high temperatures and the values Θ_p change from negative to positive.

The latter reflects a change in the nature of interactions in the subsystem of magnetic moments of chromium and copper. This circumstance is reflected in the temperature dependences of the effective magnetic moment μ_{eff}/f.u.), which, unlike that for Cr$_{0.25}$HfSe$_2$, have a non-monotonic character (Fig. 5).

The obtained the results for co-intercalated phases are difficult to explain from the point of localized and non-interacting magnetic moments. The consideration of the indirect interaction between localized moments via conduction electrons based on RKKY mechanism, which is oscillatory in nature and varies depending on the distance between magnetically active ions, also cannot explain the change in the nature of interactions with temperature changes.

Another alternative for describing magnetic properties, discussed in the literature [16–18], is the magnetism model

of collectivized electrons. It is possible that in this case, given the significant increase in the concentration of charge carriers with the additional introduction of copper, such an approach may take place. A temperature dependence of static magnetic susceptibility can be obtained, similar to Curie−Weiss law within the framework of this model, based on the idea of local spin density fluctuation (LSDF). At the same time, the temperature dependence of the amplitude of the LSDF can play an important role in the formation of the magnetic state.

4. Conclusion

Experimental data on the magnetic properties of hafnium diselenide during its separate and joint intercalation with copper and chromium atoms have been obtained. It is shown that the magnetic susceptibility of Cu_xHfSe_2 samples is well approximated by Curie−Weiss formula with a predominance of the diamagnetic component at room temperature. The increase of the paramagnetic contribution at low temperatures is, in our opinion, is attributable to the presence of divalent copper ions. Based on experimental data, the relative content of such ions in each of the Cu_xHfSe_2 compounds was estimated.

A sample of $Cr_{0.25}HfSe_2$ with an activation character of conductivity was selected as a compound with chromium. The lower values of the effective magnetic moment of chromium ions in this compound compared to the spin value may be due to the partial delocalization of $3d$-chromium electrons, as observed in many LSDF compounds intercalated with $3d$-elements [5,6,8]. The additional introduction of copper into samples intercalated with chromium leads to a significant increase in the concentration of charge carriers while maintaining the activation type of conductivity. Magnetic susceptibility also increases significantly. The dependences $\chi(T)$ for $Cu_xCr_{0.25}HfSe_2$ are also satisfactorily described by the Curie−Weiss formula. A clear dependence of the determined parameters on the choice of the temperature range of approximation was discovered for jointly intercalated compounds. Parameters such as the constant C and the value μ_{eff} decrease monotonically when the approximation interval shifts to the region of higher temperatures. In this case, the paramagnetic Curie temperature Θ_p changes sign from negative to positive along with a change of absolute value, which indicates a change of the nature of interactions in the magnetic subsystem. This result is also confirmed by the non-monotonic nature of the temperature dependences of the effective magnetic moment of these compounds.

Due to the presence of two magnetically active ions in these compounds, the effective magnetic moment was determined from experimental data per molecule of the compound (formula unit). An attempt to present this value as an additive sum of localized magnetic moments of chromium and copper, taking into account the preliminary data obtained for them, was unsuccessful. This was most evident for $Cu_{0.2}Cr_{0.25}HfSe_2$, where the experimental and calculated values differed several times. It is proposed to use various models of the formation of the magnetic state to explain the data obtained.

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Conflict of interest

The author declares that he has no conflict of interest.

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