ELECTRONIC STRUCTURE AND HYPERFINE INTERACTIONS DICHALCOGENIDES Cr_xVSe_2 ($x \leq 0.5$): ^{51}V NMR STUDY

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Abstract. A systematic study of the electronic structure of chromium-intercalated vanadium dichalcogenide CrxVSe2 ($x \leq 0.5$) was performed using X-ray diffractometry, magnetometry and nuclear magnetic resonance (NMR) spectroscopy on 51V nuclei. The values of the components of the magnetic shift tensors and the electric field gradient at the location of vanadium nuclei are determined. When chromium ions are introduced into the VSe2 matrix, the NMR spectrum on 51V nuclei widens significantly, the fine structure disappears, and the line shift changes its sign relative to the diamagnetic point. Significant local charge and spin heterogeneity of intercalated compounds has been revealed. It was found that the overlap of 3d, 4s shells of vanadium ions and chromium orbitals leads to the appearance of a positive hyperfine field induced by the magnetic moments of chromium on vanadium nuclei. Estimates of the hyperfine interaction constants on vanadium ions are made from the temperature dependences of the NMR line shift and susceptibility in CrxVSe2 ($x \leq 0.5$). In CrxVSe2 compounds ($0.1 \leq x \leq 0.5$), signs of the formation of a superstructure of chromium ion positions in the ab plane were found.

Keywords: *vanadium dichalcogenide, nuclear magnetic resonance, hyperfine field, electronic structure*

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INTRODUCTION

Currently, layered dichalcogenides of transition elements are the subject of numerous scientific studies due to the variety of physical and physicochemical properties of materials based on these compounds. Dichalcogenides have a quasi-two-dimensional crystal structure, which is a consequence of the weak Van der Waals bonding between three-layer blocks *X* - *Me* - *X* (where *X* – is a chalcogen, *Me* – is a metal from groups IV, V) [1-5]. Atoms of various elements can be intercalated between the blocks. The physical properties of materials obtained in this way differ significantly from the properties of the original dichalcogenides and demonstrate a strong dependence on both the type and concentration of intercalated atoms [4, 6-11].

One of the prominent representatives of such compounds is vanadium diselenide VSe_2. The compound VSe_2 has been fairly well studied, with interest in it due to the presence of phase transitions at low temperatures, leading to the emergence of charge density waves (CDW) in the crystalline structure of the sample [5, 12-17]. At temperatures above the transition to CDW states, $1T$-VSe_2 has mixed metallic conductivity associated with strongly hybridized s-p-d-bands [17-19].

In works [20, 21], intercalation with Na, Cs, and K atoms was studied in detail using photoemission and scanning tunneling microscopy. The alkali metal Na is an effective dopant as an electron donor with a relatively small ionic radius, which simplifies the intercalation process while preserving the structure of the main matrix. As a result, it was shown that the valence bands of the original VSe_2 matrix have a three-dimensional character, and intercalation with alkali ions Na, K, and Cs causes a transition from three-dimensional to two-dimensional character, which is largely explained by charge transfer to the matrix lattice and separation of VSe_2 layers. Moreover, it was found that the ions of intercalated sodium are unevenly distributed between the VSe_2 layers. Na ions form islands or "two-dimensional clusters," dividing the surface area into intercalated and non-intercalated regions.

According to first-principles calculations, the electronic structure of VSe_2 is dominated by $3d$-orbitals of vanadium, and the orbital decomposition shows that the peak crossing the Fermi level is mainly formed by dz^2-states of vanadium [4, 14, 19, 22]. The presented results are consistent with the trigonal antiprismatic splitting of the crystal field at the locations of vanadium ions. The distribution of electron density across different 3 *d orbitals,* calculated in work [11], predicts almost complete mutual compensation of anisotropic contributions to the hyperfine field at vanadium nuclei and isotropic behavior of the NMR magnetic shift of ^{51}V. It is also expected that dz^2-states crossing the Fermi level will be highly sensitive to interlayer interactions due to their elongated orbital shape along the out-of-plane direction. Therefore, intercalation of dopants will affect the states near the Fermi level. For example, first-principles calculations indicate a significant charge transfer between sodium atoms and the VSe_2 layer, which leads to weakening of interlayer bonding. Furthermore, the levels of $3dz^2$-electrons in doped VSe_2 shift to energy regions below the Fermi level.

Later, research interest in the intercalation of VSe_2 with alkali metals was fueled by prospects for use in sodium-potassium-ion batteries [23]. Due to the inherent metallic conductivity of VSe_2, improved sodium/potassium storage characteristics and ultra-stability of materials during cycling were demonstrated.

Fig. 1. Crystal $1T$ structure of the VSe_2 compound. The solid bold line shows the basic unit cell. Arrows indicate the areas of chromium ion intercalation.

The compounds VSe_2, intercalated with magnetic ions, are less extensively covered in the scientific literature (Fig. 1). For instance, studies [24, 25] investigated the structural characteristics, electrical and magnetic properties of vanadium diselenide samples intercalated with chromium atoms. Structural studies showed a decrease in crystal lattice symmetry from hexagonal to monoclinic with increasing concentration of intercalated atoms, caused by their ordering in the Van der Waals gap. The values of effective magnetic moments of chromium ions in Cr_xVSe_2 decrease compared to spin characteristics as the chromium content increases, and their change correlates with the concentration dependence of the c parameter of the unit cell. It has been shown that at temperatures below 30 K for compositions $x > 0.2$, the compounds transition to a spin glass state.

Unlike the well-studied VSe_2 compound, there is relatively little data in the literature on the features of the electronic structure and distribution of charge and spin density in Cr_xVSe_2 compounds based on vanadium diselenide intercalated with Cr atoms. Considering that this compound is similar to the Cr_xNbSe_2 compounds that we have systematically studied previously [8, 26-28], it is important to investigate the patterns of properties and ordering of internalized compounds with different matrices.

SAMPLES AND RESEARCH METHODS

The polycrystalline samples were sintered pressed tablets of fine-grained powders. The compounds were synthesized by the solid-phase ampoule synthesis method. A two-stage technology was used to prepare Cr_xVSe_2 ($0 \delta x \delta 0.5$) samples. In the first stage, the VSe_2 matrix was prepared, and in the second stage – the intercalated compound Cr_xVSe_2. The starting materials were granulated selenium (Se) grade OSCh 22-4 (purity 99.9996%), chromium (Cr) metal in plates (purity 99.95%), vanadium (V) electrolytic metal grade VEL-1 (purity 99.95%). The synthesis details and structural parameters of the compound are similar to those given in [24, 29].

X-ray diffraction analysis of the obtained samples was carried out on a Bruker D8 ADVANCE diffractometer in Cu $K\alpha$-radiation. Structure refinement and determination of structural parameters were performed using the FullProf software package. X-ray structural analysis of the polycrystalline VSe_2 sample showed that the compound has a layered trigonal crystal structure and is described by the space group $P\bar{3}m1$ with unit cell parameters $a_0 = 3.350(9)$ Å, $c_0 = 6.100(2)$ Å ($\alpha = \beta = 90°$, $\gamma = 120°$). These values are in good agreement with previously obtained results in works [24, 29]. Figure 2 shows the behavior of parameters a, b, c and the unit cell volume in the compound Cr_xVSe_2 depending on the concentration of chromium ions x.

Fig. 2. a) Behavior of parameters a, b, c and b) unit cell volume in compounds Cr_xVSe_2 depending on the concentration of chromium ions x at room temperature.

The compound $Cr_{0.1}VSe_2$ is isostructural to the VSe_2 matrix, has a trigonal crystal structure, and the X-ray diffraction pattern is also processed in the trigonal system with the space group $P\bar{3}m1$. It was found that with an increase in concentration to $x = 0.33$, 0.5 in the subsystem of intercalated chromium atoms, orderings of the type $\sqrt{3}a_0 \times a_0 \times 2c_0$ and $2\sqrt{3}a_0 \times b_0 \times c_0$ are formed, respectively. In the compound $Cr_{0.5}VSe_2$ no more than 2% of vanadium oxide V_2O_3 is observed, while no foreign phases were detected in other studied compounds.

The susceptibility studies of the samples were performed on a MPMS setup (Quantum Design, USA) in the temperature range from 2 K to 330 K.

NMR measurements on ^{51}V nuclei were performed on a pulse spectrometer in an external magnetic field $H_0 = 92.8$ kOe in the temperature range from 20 to 300 K. To eliminate NMR signals from metallic copper, a silver resonance coil was used. NMR spectra on ^{51}V nuclei were obtained using the standard spin echo technique $p - t_{del} - 2p - t_{del} - echo$. The duration of the first pulse was chosen as $p = 1$ μs, and the power of the radio frequency amplifier as $N = 300$ W. The delay between pulses was $t_{del} = 20$ μs. The NMR spectra on ^{51}V nuclei presented in this work are the sum of Fourier transforms of the obtained *echo* signals accumulated in the required frequency range with a step of $\Delta\nu = 100$ kHz. For modeling the NMR spectra, an original program "Simul"

[30] was used, which allows numerical calculation of the line shape based on the complete Hamiltonian of the nuclear system, taking into account Zeeman and quadrupole contributions [31, 32]. The line shifts of NMR on ^{51}V nuclei, $K = (\nu - \nu_0)\times100/\nu_0$, were determined relative to $\nu_0 = {}^{51}\gamma \cdot H_0$.

RESULTS AND DISCUSSION

Characteristic NMR spectrum of ^{51}V nuclei in the initial polycrystalline matrix sample of VSe_2, obtained at $T = 150$ K in an external magnetic field $H_0 = 92.8$ kOe, is presented in Fig. 3. The nucleus of the ^{51}V isotope has a spin $^{51}I = 7/2$ and an electric quadrupole moment $e\,^{51}Q = -0.0515 \times 10^{-24}$ cm^2. In this case, the NMR spectrum represents a set of $2I = 7$ lines, one of which corresponds to the central transition $m_{-1/2 \leftrightarrow +1/2}$, and the other six to satellite transitions $m_{\pm3/2 \leftrightarrow \pm 1/2}$, $m_{\pm5/2 \leftrightarrow \pm 3/2}$, $m_{\pm7/2 \leftrightarrow \pm 5/2}$. This spectral structure is due to the interaction of the nuclear quadrupole moment with the electric field gradient (EFG) created at the location of the nuclei by their charge environment [12, 15, 16, 31, 32]. When modeling the ^{51}V NMR spectrum at room temperature, values of the quadrupole frequency $\nu_Q = 364$ (1) kHz and asymmetry parameter $\eta = 0.0(1)$ were obtained, which define the EFG tensor in VSe_2. As can be seen from Fig. 3, the experimental spectrum is satisfactorily described by a single line with one set of parameters, indicating the equivalence of all vanadium nuclear positions in the structure. The inset of Fig. 3 shows the temperature dependence of the quadrupole frequency ν_Q. It can be seen that in the temperature range from 300 K to 100 K, there is a slight increase in ν_Q, which is apparently related to the decrease in both thermal fluctuations of atoms and interatomic distances.

Fig. 3. NMR spectrum of ^{51}V nuclei in VSe_2 in an external magnetic field $H_0 = 92.8$ kOe at a temperature of $T = 150$ K. The dashed line (red color) – modeling of the experimental NMR spectrum with a single line. The inset shows the temperature dependence of the quadrupole frequency ν_Q of vanadium in VSe_2.

Figure 4 shows the temperature dependence of magnetic susceptibility $\chi(T)$ for VSe_2. In the region $T < 110$ K, a sharp decrease in susceptibility is observed, which is associated with the formation of a charge density wave, and a rapid increase in $\chi(T)$ below $T < 25$ K.

Fig. 4. Dependence of magnetic susceptibility of VSe_2 on temperature and approximation of the low-temperature part of the data by the Curie-Weiss relationship.

This behavior of magnetic susceptibility is discussed in detail in works [12, 16, 17, 33].

It should be noted that in the structure of VSe_2 self-intercalation processes or the exit of vanadium ions from the regular lattice to interlayer positions with the formation of vacancies are possible. This is due to the fact that octahedra of selenium ions are structurally equivalent both within the layer and between layers. Previous magnetic studies of VSe_2 showed that excess V atoms intercalated between layers possess localized magnetic moments $\mu = 2.5\ \mu_B$ [33]. Following the reasoning in works [12, 17], one can estimate the number of vanadium ions that get between the layers of VSe_2. This can be done using the temperature dependence of susceptibility $\chi(T)$ below $T = 25$ K, which is well described by the Curie-Weiss law:

$$\chi(T) = \chi_0 + C/(T - \Theta), \qquad (1)$$

where C – is the Curie constant, χ_0 is the temperature-independent susceptibility of VSe_2 layers.

According to band structure calculations [19, 34], the conduction band of VSe_2 is formed mainly by *d* -states. The negative shift of the NMR line on ^{51}V nuclei ($^{51}K < 0$), as will be shown below, also indicates the presence of 3 *d* -states of the vanadium ion at the Fermi level. Therefore, the main contributions to χ_0 are the *d* -spin (χ_d) and *d* -orbital (χ_{orb}) susceptibilities, as well as the diamagnetic susceptibility of the ionic cores (χ_{dia}):

$$\chi_0 = \chi_d + \chi_{orb} + \chi_{dia} . \quad (2)$$

Approximation of the experimental data by the Curie-Weiss law in the range from 4.2 to 25 K with a constant value of χ_0 , allowed to obtain the constant $C = 7.8 \cdot 10^{-4}$ cm ^{3} K/mol. Using this value and assuming that the magnetic moment of the vanadium atom $\mu = 2.5\ \mu_B$ [33], we estimated the concentration of interstitial V atoms, which in our sample was 0.001.

Considering that the NMR spectrum of vanadium nuclei is described by a single line, and the concentration of interlayer vanadium ions is only about 0.1%, it can be concluded that the NMR experiment provides information about the electronic state of vanadium ions only in the main VSe_2 matrix. We will take this fact into account in our further discussion of the results of the study of chromium-intercalated compounds Cr_xVSe_2 ($x \leq 0.5$). The temperature dependence $\chi(T)$, obtained by subtracting the Curie-Weiss contribution from the experimental data, is also shown in Fig. 4. The only term in $\chi(T)$ that is expected to strongly depend on temperature – is the spin susceptibility χ_d , which is proportional in the first approximation to the density of states at the Fermi level $N(E_F)$. Consequently, the decrease in χ_0 below 110 K can be explained by a decrease in $N(E_F)$ during the phase transition to the charge density wave state.

Fig. 5. NMR spectrum of Nuclear magnetic resonance ^{51}V nuclei in Cr_xVSe_2 ($x = 0$; 0.10; 0.33; 0.50) in an external magnetic field $H_0 = 92.8$ kOe at temperature $T = 295$ K.

Fig. 5 shows the characteristic NMR spectra of ^{51}V nuclei at room temperature for the compounds Cr_xVSe_2 ($x \leq 0.5$). It can be seen that when chromium ions are introduced into the VSe_2 matrix, the fine structure of the NMR spectrum disappears, the NMR line significantly broadens, and the average line shift $K(T)$ changes from negative to positive values. Obviously, such significant changes in the NMR spectra indicate the appearance of local inhomogeneities, both charge and magnetic, arising from the introduction of chromium ions. Each NMR spectrum of ^{51}V nuclei in the temperature range 20 K $\leq T \leq$ 300 K is satisfactorily described by a Gaussian line shape.

Fig. 6. Dependence of the half-width at half-height of the NMR spectrum on ^{51}V nuclei in Cr_xVSe_2 ($x = 0$; 0.10; 0.33; 0.50) on temperature.

Temperature dependences of the half-width at half-height $\delta(T)$ of NMR spectra on ^{51}V nuclei and the line shift $K(T)$ are presented in Fig. 6 and Fig. 7. The appearance of exponential behavior of $\delta(T)$ and line shift $K(T)$ is associated with the spin magnetism of Cr ions in the structure of Cr_xVSe_2 ($x \leq 0.5$).

Fig. 7. Dependence of the NMR line shift on ^{51}V nuclei in Cr_xVSe_2 ($x = 0$; 0.10; 0.33; 0.50) on temperature.

In our work [26], from the evolution of NMR spectra on ^{93}Nb nuclei in the paramagnetic region of compositions Cr_xNbSe_2 ($x \leq 0.5$), it was shown that the spectra clearly separate into three lines with different shifts and quadrupole interaction parameters. Analysis of NMR spectra on ^{93}Nb nuclei allowed detecting the presence of three magnetically non-equivalent niobium positions in

Cr_xNbSe_2, with 0, 1, and 2 chromium ions in their immediate surroundings, respectively. In the Cr_xVSe_2 system, a clear separation of NMR spectra on ^{51}V nuclei into separate lines is not observed. This indicates that there is significant local magnetic disorder in the Cr_xVSe_2 system. On the other hand, the ^{51}V spectra represent an almost Gaussian distribution throughout the entire temperature range (20 K $\leq T \leq$ 300 K). This indicates that all vanadium ions in the structure are in a sufficiently similar electronic state, i.e., the electron density is distributed uniformly regardless of the concentration of chromium ions.

The task of determining the magnetic state of chromium ions can be solved using NMR methods on ^{53}Cr nuclei in a local magnetic field at low temperatures. According to magnetometry data in Cr_xVSe_2 ($0.1 \leq x \leq 0.5$), transitions to a spin or cluster glass state are observed. However, the NMR frequency on ^{53}Cr nuclei in the local magnetic field at the nucleus location was expected to be in a range.

However, after scanning the frequency range of 20-70 MHz, characteristic for magnetic chromium ions [27, 35, 36], the NMR signal could not be detected. It is well known that the observation of magnetic resonance on the nuclei of a magnetic ion is usually hampered by very short spin-spin relaxation times. In the case of chromium, an additional factor complicating the detection of the NMR signal is the low natural abundance of the NMR isotope ^{53}Cr (9.5%).

At $T > T_C$ the NMR line shift has the form $K = K_0 + C_{NMR}/(T - \theta\ \theta)$, where K_0, C_{NMR}, ⎩ - are constants, i.e., it contains a Curie-Weiss contribution. The magnetic shift of the NMR line on ^{51}V $K(T)$ nuclei in Cr_xVSe_2 can be written as three major contributions:

$$K(T) = K_s + K_{\mathrm{orb}} + K_s^{\mathrm{CW}}(T)\ . \qquad (3)$$

The first term in expression (3) $K_s = \left(H_{\mathrm{c}} + H_{\mathrm{cp}}\right)$ represents the contribution from conduction electrons. Here H_c and H_{cp} are isotropic constants of the Fermi contact interaction and core polarization, respectively. The contact contribution to the hyperfine interaction H_c is caused by the hyperfine interaction of the nuclear spin with valence s-electrons. It is positive and typically significant in metals. The term H_{cp} describes the hyperfine interaction (HFI) caused by the polarization of filled s-shells of the ion by unpaired d-electrons. This contribution is isotropic and, with rare exceptions, negative [37]. $?_s$ – the temperature-independent Pauli spin susceptibility of conduction electrons. The second contribution, orbital K_{orb}, shift is due to the van Vleck paramagnetism of valence d-electrons of the ion. It arises due to partial unfreezing of the orbital momentum in an external magnetic field, is temperature-independent and is positive. Finally, the third term in (3) $K_s^{\mathrm{CW}}(T)$ is caused by localized magnetic moments (LMM) of d-electrons of chromium. This contribution is induced by the magnetic field created on vanadium nuclei from LMM of neighboring Cr ions. This contribution can be written as: $K_s^{\mathrm{CW}}(T) = \frac{H_{tr}}{\mu_{\mathrm{B}}} ?_s^{\mathrm{Cr}}(T)$, where H_{tr} – induced hyperfine field (HFF) from neighboring chromium ions. It is mainly determined by the degree of overlap of chromium d-orbitals with orbitals of neighboring vanadium ions.

Thus, we can represent the shift $K(T)$ in the form of temperature-dependent and temperature-independent parts:

$$\mathrm{K}(T) = \frac{H_{\mathrm{tr}}}{\mu_{\mathrm{B}}} \chi_s^{\mathrm{Cr}}(T) + K_0, \qquad (4)$$

where $K_0 = K_s + K_{\mathrm{orb}}$.

In turn, the uniform magnetic susceptibility χ *(T)* also consists of two main terms: temperature-dependent according to the Curie-Weiss law spin susceptibility $\chi_s^{\mathrm{Cr}}(T)$ and temperature-independent $\chi_0 = \chi_s + \chi_{\mathrm{orb}}$:

$$\chi(T) = \chi_s^{\mathrm{Cr}}(T) + \chi_0. \tag{5}$$

Using expressions (4) and (5), one can obtain the dependence of the shift *K* (*T*) on χ (*T*) with temperature as a parameter:

$$\mathrm{K}(\chi) = \frac{H_{\mathrm{tr}}}{\mu_{\mathrm{B}}}\chi - \frac{H_{\mathrm{tr}}}{\mu_{\mathrm{B}}}\chi_0 + K_0. \tag{6}$$

Such parametric dependencies *K* (χ) for $\mathrm{Cr}_x\mathrm{VSe}_2$ ($x \leq 0.5$) samples are presented in Fig. 8. As we can see, these dependencies are well approximated by straight lines. Then the HFI can be easily calculated from the tangents of the angles formed by these lines with the abscissa axis. The values of hyperfine field , induced from chromium on vanadium atoms, are H_{tr} ($x = 0.1$) = 1.6 kOe/ μB , H_{tr} ($x = 0.33$) = 7.7 kOe/ μB , H_{tr} ($x = 0.5$) = 11.0 kOe/ μB .

Fig. 8. Dependence of NMR line shift *K* on ^{51}V nuclei in $\mathrm{Cr}_x\mathrm{VSe}_2$ ($x = 0.10; 0.33; 0.50$) on magnetic susceptibility χ . Straight lines are the result of approximating the data with function (4). H_{tr} – constant of hyperfine induced interaction. The inset shows the *K* – χ diagram for the initial composition VSe_2 .

Regarding the initial composition VSe_2 , the situation is slightly different. For it, in expression (3), the third contribution is absent, but due to the emergence of the CDW state, the contribution $K_s = \left(H_{\mathrm{c}} + H_{\mathrm{cp}}\right)$ becomes temperature-dependent below 100 K. In this case, the parametric dependence (5) takes the following form:

$$\mathrm{K}(\chi) = \frac{\mathrm{H_c + H_{cp}}}{\mu_{\mathrm{B}}}\chi - \frac{\mathrm{H_{orb}}}{\mu_{\mathrm{B}}}\chi_{\mathrm{orb}} + \mathrm{K_{orb}}. \tag{7}$$

This dependence is presented in the inset of Fig. 8. Approximation of this dependence by a straight line gives for the sum $H_{\mathrm{c}} + H_{\mathrm{cp}}$ a value of –67(2) kOe/ μB . The negative value of this sum indicates that the contribution to the HFI on vanadium nuclei in VSe_2 from core polarization prevails over the contribution from the valence 4 *s* -electrons of this ion.

When chromium ions are intercalated into the original VSe_2 system, additional electrons are added. Thus, for the composition $x = 0.1$, this is $n = 0.3$ electrons per formula unit, $n = 0.99$ for the composition $x = 0.33$, and $n = 1.5$ for the composition $x = 0.5$. That is, electronic doping of the matrix VSe_2 -layers occurs. In the $\mathrm{Cr}_x\mathrm{VSe}_2$ system, all electronic shells of Se^{2+} ions are filled ($3d^{10}4s^24p^6$) and they cannot acquire additional electrons. Therefore, to fulfill the condition of electroneutrality, vanadium ions in $\mathrm{Cr}_x\mathrm{VSe}_2$ acquire an effective fractional valence $\mathrm{V}^{(4\text{-n})+}$. Indeed, it is well known that the vanadium ion in materials can have several chemical valence states: V^{5+} V^{4+} , V^{3+} , V^{2+} (from $3d^04s^0$ to $3d^34s^0$). We assume that all electrons doped into the matrix enter the conduction band, i.e., remain delocalized. Otherwise, if they were localized in the 3 *d* -orbitals of vanadium, with electronic doping, an additional shift of the NMR ^{51}V line would be observed toward negative values (localized *d* -electrons increase the negative contribution of core polarization to the CTS). In reality, the situation is the opposite: with increasing *x* , the NMR line shift *K* becomes positive. As can be seen from Fig. 7, upon intercalation of VSe_2 with chromium, a significant Curie-Weiss contribution appears in the *K* (*T*) dependence. This contribution may be due to an induced magnetic field from localized magnetic moments of chromium due to the overlap of *d* -orbitals of Cr $^{3+}$ ions with orbitals of vanadium ions. In this case, overlap with the free 4 *s* -shell will lead to a positive shift, while overlap with the 3 *d* -orbital will lead to a negative one. Thus, to explain the emergence of an additional positive shift of the NMR line on ^{51}V nuclei during the intercalation of VSe_2 with chromium, we must assume that in addition to 3 *d* -orbitals, 4 *s* -orbitals of vanadium ions also participate in the formation of the V-Cr bond. Unfortunately, we cannot estimate the degree of overlap of 3 *d* -orbitals of Cr with 3 *d and* 4 *s* -orbitals of V, since, as mentioned above, these overlaps give different signs for magnetic fields induced on vanadium nuclei, i.e., these fields partially compensate each other. The degree of overlap can be quite high, similar to that which occurs in the related system Cr_xNbSe_2 [26-28, 38].

Below the critical temperature, a state like spin or cluster glass is formed [24]. The absence of long-range magnetic order in Cr_xVSe_2 compounds distinguishes them from a number of other similar systems intercalated with chromium. In particular, such as Cr_xTiSe_2, in which at $x > 0.33$ an antiferromagnetic order is realized [39]. Also from compounds $Cr_{0.33}NbSe_2$ and $Cr_{0.65}TiTe_2$, in which ferromagnetic ordering of chromium magnetic moments is observed [8, 24]. The reason for this may be the difference in the degree of hybridization of Cr and transition metal orbitals in the matrix and, as a consequence, in the degree of localization of 3 *d electronic* states of chromium. In turn, the degree of hybridization depends on the distances between the matrix layers. Therefore, it can be stated that the host compound plays a dominant role in the formation of the magnetic state of intercalated compounds.

CONCLUSION

For the first time, an NMR study of Cr_xVSe_2 ($x \leq 0.5$) was performed in the paramagnetic state using ^{51}V nuclei as NMR probes. The values of the components of the magnetic shift tensors and electric field gradient at the location of vanadium nuclei in the VSe_2 matrix were determined. When chromium ions are introduced into the VSe_2 structure, the NMR spectrum broadens, the fine structure disappears, and the NMR line shift on the ^{51}V nuclei changes its sign relative to the diamagnetic point.

A significant local charge and spin inhomogeneity of intercalated compounds is shown. The presence of a non-zero positive hyperfine field induced from 3 *d* -electrons of chromium on vanadium nuclei was revealed, which indicates an overlap of 3 *d and* 4 *s shells* of vanadium ions with the orbitals of the magnetic ion.

Analysis of NMR spectra on ^{51}V nuclei does not reveal the presence of three magnetically non-equivalent vanadium positions in Cr_xVSe_2, as was observed in the Cr_xNbSe_2 system on ^{93}Nb nuclei. In Cr_xVSe_2 compounds ($0.1 \leq x \leq 0.5$), signs of the formation of a superstructure of chromium ion positions in the ab plane were discovered.

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CONFLICT OF INTERESTS

The authors of this work declare that they have no conflict of interest.

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