CHARGE AND SPIN DENSITY DISTRIBUTION IN VSe_2 DICHALCOGENIDE ACCORDING TO NMR ^{51}V DATA

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Abstract. A polycrystalline sample of VSe_2 was studied using magnetometry and nuclear magnetic resonance (NMR) spectroscopy on ^{51}V nuclei. The values of the components of the magnetic shift tensors and the electric field gradient (EFG) at the location of vanadium nuclei were determined from the processing of the NMR spectra recorded in the range from 300 K to 10 K. It was found that the valence contribution to the EFG is opposite to the lattice contribution. At temperatures below $T_0 \approx 110$ K, the ^{51}V NMR line undergoes significant inhomogeneous broadening, which is associated with a transition to a state with a charge density wave (CDW). From the data on the ^{51}V NMR line broadening, changes in the quadrupole frequency ν_Q across the crystal were determined, which is a characteristic of the charge density distribution near the ^{51}V nuclei. A combined analysis of the temperature dependences of the NMR line shift and magnetic susceptibility allowed us to estimate the hyperfine magnetic fields (HFF) on vanadium nuclei in VSe_2 in the CDW state. An estimate was obtained for the difference in spin polarization of various 3*d*-orbitals of the V ion, which corresponds to the density of electron states with an energy slightly below the Fermi level.

Keywords: *charge density wave, NMR spectroscopy, charge distribution, spin distribution, dichalcogenide*

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INTRODUCTION

The diversity of physical and chemical properties of layered transition metal dichalcogenides and the improvement of sample synthesis technologies are driving increasing researcher attention to this class of compounds. Common to the entire class is a pronounced quasi-two-dimensional crystalline structure with weak bonding between the three-layer X-M-X blocks (where X - chalcogen, M - metal). The materials under consideration have a large number of possible structural polytypes [1]. In such layered structures, chalcogen and metal atoms form hexagonal planes, with two possible types of coordination for metal atoms. In the first case, six chalcogen atoms form an octahedron, and in the other, a trigonal prism (Fig. 1a, b) [2-4].

Fig. 1. Two types of metal atom coordination by chalcogen atoms: (a) VSe_2-octahedral and (b) $NbSe_2$-trigonal prismatic; (c) fragment of the crystal structure of VSe_2.

Furthermore, the weak interplanar interaction allows for various arrangements of the MX_6 structural blocks in the crystal along the axis perpendicular to the hexagonal layers (axis *c* in Fig. 1). In this work, we studied a VSe_2 sample with a 1T structure, shown in Fig. 1c, in which triads of selenium atoms from two adjacent planes form an octahedron.

Initially, interest in dichalcogenides was driven by the possibility of intercalating atoms between the layers of the main matrix and the prospect of controlling the physical properties of the material. Current interest is more related to the emergence of technologies for synthesizing ultrathin and even monolayer samples [5-7]. In this respect, VSe_2 is no exception [8, 9]. Increasingly stringent requirements for device miniaturization in modern spintronics, microelectronics, optics, and sensor technology lead to the need to search for functional materials with a thickness of one or several atomic layers. Thus, transition metal dichalcogenides can be considered as an alternative to functional materials based on graphene.

Vanadium diselenide VSe_2 is one of the most prominent representatives of compounds in its class, which to date has been the subject of a large number of both experimental and theoretical studies [8-14]. The reason for the unwavering interest since the 1970s is the well-established presence of a charge density wave (CDW) state in VSe_2, as well as the recent discovery of ferromagnetism in monolayer samples at room temperature [8-10]. Among the most accurate methods for studying CDW states are nuclear magnetic resonance (NMR) methods. Nuclei with nuclear spin $I > 1/2$ and quadrupole moment eQ, serve as natural probes for detecting charge ordering near the nucleus through the interaction of the quadrupole moment with the electric field gradient (EFG). Such probe nuclei in VSe_2 are ^{51}V nuclei, which have spin $^{51}I = 7/2$ and quadrupole moment $e\,^{51}Q = -0.0515\cdot10^{-24}$ cm^2, which allows to investigate local electric and magnetic fields at their positions in VSe_2 at the center of an octahedron of selenium atoms.

The compound VSe_2 has already been studied by NMR methods on ^{51}V nuclei [14, 16-18]. One of the important conclusions of the early studies was the discovery of incommensurate CDW. However, in the literature we did not find detailed temperature dependencies of the shapes of NMR spectral lines on ^{51}V nuclei obtained on VSe_2 polycrystal. Additionally, the shapes of spectral lines obtained on a single crystal were analyzed for changes in charge order, without taking into account possible changes in spin densities in the crystal.

The spectrum obtained on powder, unlike a single crystal, provides information about the local magnetic and charge densities in a solid, taking into account all possible directions of the magnetic field relative to the crystal axes. Modern methods of obtaining and processing experimental data, compared to the 1980s, allow for the analysis of complex spectral lines, including lines in samples with incommensurate order [19-21]. Additionally, today the literature contains detailed data of electron density of states calculations from first principles for both VSe_2 [10, 22, 23] and other dichalcogenides [24], which simplifies the interpretation of NMR data.

SAMPLES AND RESEARCH METHODS

Research results on VSe_2, obtained in different studies, often diverge, particularly the values of magnetic susceptibility, as well as the CDW vector magnitudes, do not coincide [12, 13]. One of the reasons for such discrepancies may be the difference in the stoichiometry of samples used in various works, which is related to the wide homogeneity range of vanadium diselenide ($VSe_{1.62}$ - $VSe_{1.97}$) and the strong dependence of the compound's composition on the synthesis temperature. Differences when using various synthesis conditions may be associated with the fact that annealing at elevated temperatures leads to self-intercalation of VSe_2 with vanadium atoms. In this case, the synthesis product is described by the formula $V_xV_{1\text{-}y}{}_ySe_2$, where x represents V atoms intercalated between the three-layer Se-V-Se blocks, y represents vacancies in the vanadium layer. Detailed methods of synthesis and certification of the investigated samples are provided in [25].

Fig. 2. Temperature dependence of magnetic susceptibility of the VSe_2 sample synthesized at 580°C, and the approximation of the low-temperature part of the data with the Curie-Weiss relationship. The inset shows susceptibility data for the VSe_2 sample synthesized at 800°C.

The difference in the properties of VSe_2 samples obtained under different conditions is clearly manifested in the behavior of magnetic susceptibility (Fig. 2). Studies of sample susceptibility were performed on a MPMS system (Quantum Design, USA) in the temperature range from 2 K to 330 K.

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. Such behavior of magnetic susceptibility is discussed in detail in papers [14, 17, 26]. At low temperatures, magnetometry data for both samples demonstrate the presence of a Curie-Weiss contribution to the magnetic susceptibility. In the VSe_2 (800°C) sample, this contribution is predominant. Such a difference in susceptibility behavior can be explained by the difference in the degree of self-intercalation of the samples and the presence of vanadium ions with localized magnetic moment [26]. In this case, the VSe_2 (580°C) sample has higher stoichiometry, in which the contribution from self-intercalation defects to the total magnetic susceptibility manifests at temperatures below 25 K. Thus, synthesis conditions significantly affect the composition of the obtained materials and, consequently, their physical properties. In this work, we investigated the VSe_2 sample synthesized at 580°C with an estimated concentration of interstitial vanadium ions of 0.1%. For the sample synthesized at a temperature of 800°C, a similar estimate of the concentration of self-intercalated vanadium ions is 2%.

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 10 to 300 K. NMR spectra were obtained using the standard spin echo technique $p - t_{\text{del}} - 2p - t_{\text{del}}$–echo. The duration of the first pulse was chosen as $p = 1$ μs, the power of the radio frequency amplifier $N = 300$ W. The delay between pulses $t_{del} = 20$ μs. The NMR spectra on ^{51}V nuclei presented in this work are the sum of Fourier transforms of echo signals accumulated in the required frequency range with a step $\Delta\nu = 100$ кГц. For modeling the NMR spectra, the original program "Simul" [27] was used, which allows numerical calculation of the line shape based on the full Hamiltonian of the nuclear system, taking into account Zeeman and quadrupole contributions. The NMR line shifts on the ^{51}V nucleus, $K = (\nu - \nu_0) \times 100 / \nu_0$, were determined relative to $\nu_0 = {}^{51}\gamma / 2\pi \cdot H_0$, where $^{51}\gamma$ is the gyromagnetic ratio of the ^{51}V nucleus.

RESULTS AND DISCUSSION

CHARGE DISTRIBUTION

The NMR spectrum of ^{51}V nuclei, obtained on a polycrystalline sample of VSe$_2$ at a temperature of $T = 116$ K in an external magnetic field $H_0 = 92.8$ kOe, is presented in Fig. 3.

Fig. 3. NMR spectrum of ^{51}V, measured at a temperature $T = 116$ K in an external magnetic field $H_0 = 92.8$ kOe. The blue dotted line is the result of modeling the spectrum with a theoretical curve. The dashed line indicates the frequency corresponding to zero shift.

The spectrum is a set of $2I = 7$ lines, one of which corresponds to the central transition –1/2 ↔ +1/2, and the other six – to satellite transitions ±3/2 ↔ ±1/2, ±5/2 ↔ ±3/2, ±7/2 ↔ ±5/2. This spectrum structure is due to the interaction of the nuclear quadrupole moment with the EFG created at the location of the nuclei by their charge environment [28, 29]. As can be seen from the figure, the experimental spectrum is satisfactorily described by a single line with one set of parameters, which indicates the equivalence of all vanadium nuclei positions in the structure. A separately observed peak of very low intensity at a frequency of 102.95 MHz corresponds to the resonance frequency of ^{27}Al nuclei, apparently contained in the sample holder in the NMR probe.

Considering the low concentration of self-intercalation defects, we can conclude that the NMR experiment provides information about the state of vanadium ions in the main VSe$_2$ matrix. The NMR frequency for satellites in the first order of perturbation theory is determined as follows [30]:

$$\nu_{m\leftrightarrow m-1} = \nu_0 + \frac{\nu_Q}{2}\left(m - \frac{1}{2}\right) \times\times \left(3\cos^2\theta - 1 + + \eta\sin^2\theta \cdot \cos 2\varphi\right), \qquad (1)$$

where ν_0 – is the frequency of the central transition line, $\nu_Q = 3e^2qQ/2I(2I-1)h$ – quadrupole frequency, m – magnetic quantum number, $\eta = |V_{xx} - V_{yy}|/V_{zz}$ – asymmetry parameter, angles φ and θ define the direction of the external magnetic field relative to the principal axes of the EFG tensor. It should be noted that the spectra were modeled taking into account higher orders of perturbation theory approximation [30]. According to studies performed on single-crystal samples [15, 17], the principal axis of the EFG tensor coincides with the *c* axis of the crystal. Taking this into account, the theoretical curve used for processing in Fig.3 was constructed with the following approximation parameters: $\nu_Q = 370$ кГц, $\eta = 0$. The obtained data are in good agreement with those previously obtained in works [14, 15, 17], which is additional evidence of the correct determination of the direction of the principal axes of the tensor relative to the crystal axes and the axial symmetry of the EFG.

The broadening of the central transition lines and satellites corresponds to a Gaussian function with a relatively small and, more importantly, the same value at half intensity $\Delta\nu \approx 20$ кГц.

Fig. 4. NMR spectra ^{51}V obtained in the temperature range from 10 to 300 K.

Figure 4 shows temperature-induced changes in the shape of the NMR spectral lines of ^{51}V recorded in the range from 10 to 300 K.

At temperatures above the transition temperature of the sample to the CDW state ($T_0 \approx 110$ K), no significant changes in the spectrum shape occur. The line remains predominantly symmetrical relative to the central transition. At temperatures below T_0 a noticeable broadening and complication of the spectra are observed. The spectra become asymmetric relative to the central transition line, shifting to higher frequencies.

Figure 5 shows the spectrum recorded at a temperature of $T = 10$ K and its modeling with a theoretical curve.

Fig. 5. NMR spectrum of ^{51}V and its modeling with a theoretical curve.

For all spectra obtained below T_0, there is a noticeable difference in the line broadening of the central transition ($\Delta\nu_{\mathrm{ct}}$) and satellites ($\Delta\nu_{\mathrm{sat}}^{m}$), which indicates a significant inhomogeneity of the charge distribution near the vanadium nuclei in the studied sample. It is obvious that the emerging charge inhomogeneity is associated with the CDWs forming in VSe $_2$ below T_0, and their contribution to the quadrupole frequency $(\Delta\nu_{\mathrm{Q}})$. It is important to note that this additional contribution will have different effects on the broadening of different pairs of satellites. Indeed, when accounting for a possible distribution in the form of ($\nu_{\mathrm{Q}} \pm \Delta\nu_{\mathrm{Q}}$) in expression (1), multipliers 3, 2, 1, 0, 1, 2, 3 will appear before the additional term in accordance with the values of m : 7/2 $\leftrightarrow$ 5/2, 3/2 $\leftrightarrow$ 1/2, –1/2 $\leftrightarrow$ –3/2, –5/2 $\leftrightarrow$ –7/2, which is reflected in the NMR spectra (Fig. 5) [29]. The experimental spectra were processed by summing the contributions of the central transition and individual pairs of satellites. The central transition line, to a first approximation, does not experience additional broadening associated with charge inhomogeneity, which allows separating the magnetic and charge contributions. Quadrupole line broadening $\Delta\nu_{\mathrm{Q}}$ in the CDW state:

$$\Delta\nu_{\mathrm{Q}} = \frac{2(\Delta\nu_{sat}^{m} - \Delta\nu_{ct})}{m - \frac{1}{2}} = 60 \text{ кГц}. \tag{2}$$

Figure 6 shows the dependence of the quadrupole frequency on temperature, obtained from the analysis of the spectra shown in Fig. 4.

Fig. 6. Temperature dependence of the quadrupole frequency obtained from the analysis of spectral lines. The inset shows the temperature dependence of the line broadening of the central transition and the first pair of satellites ($\Delta\nu_{\mathrm{sat}}^{3/2}$).

From the figure it is seen that when the temperature decreases from 300 to 100 K, the quadrupole frequency experiences a small monotonic increase. Similar dependencies of the quadrupole frequency were observed in works [31-33] and such behavior was associated with a decrease in thermal fluctuations of atoms and atomic distances. The low-temperature part corresponding to the state of the sample with CDW is of greater interest. A sharp increase in frequency is observed in the dependence when the temperature decreases, indicating significant changes in the local charge environment of vanadium nuclei. Since the EFG at the nucleus is generally determined by the vector sum of valence and lattice contributions ($(1-\gamma_\infty)\mathbf{q_v} + (1-R)\mathbf{q_c}$), the result requires additional analysis.

The lattice contribution to the EFG $\mathbf{q_c}$ with known parameters of the crystal lattice can be calculated relatively simply [34]. According to our estimates in VSe $_2$ at the nuclei ^{51}V it corresponds to $^{51}\nu_{\mathrm{Q}}^{c} \approx$ 1 МГц (with the value of the antishielding coefficient $\gamma_\infty = -9.08$ [35]). Considering the relatively small quadrupole moment of ^{51}V nuclei, the obtained value $^{51}\nu_{\mathrm{Q}}^{c}$ is quite large, which, however, is expected for a crystal with pronounced 2 D -symmetry. The lattice contribution to the EFG at the ^{51}V nuclei is formed mainly by the sublattice of positive vanadium ions, since the negative selenium ions form octahedra with a relatively small field gradient in the center (Fig. 1). The value $^{51}\nu_{\mathrm{Q}}^{c}$ is more than twice the value ν_{Q} obtained in the experiment, which clearly indicates that $\mathbf{q_v}$ and $\mathbf{q_c}$ in the structure of VSe $_2$ have opposite directions. The V $^{+4}$ ion has one valence electron, which, in general, can be in 4 s - or 3 d -state. An electron in a spherically symmetric 4 s -orbital does not create an EFG at the nucleus; the cause of $\mathbf{q_v}$ is the electron density on the 3 d -orbital.

We have made an assessment of the possible valence contribution to the nucleus ^{51}V, created by a single electron in the 3 d - state, similar to what was done in work [36] with $\langle r^{-3}\rangle = 3.67$ a.u., corresponding to the V ion [37]:

$$ {}^{51}\nu_{3d}^{v} = \frac{\frac{4}{7}3e^2q\langle r^{-3}\rangle}{h\cdot 2I(2I-1)} = 1.82\ \text{МГц}. \quad (3) $$

It should be noted that these estimates are very approximate, but they give an idea of the possible ratio of valence and lattice contributions to the ^{51}V nuclei in VSe$_2$. It is well known that the studied sample has metallic conductivity [14, 25, 38], while according to first-principles calculations [10], 3 *d* - electrons in all five possible orbital states may be found near the Fermi level. At the same time, the local environment of the V atom can lead to a trigonal-antiprismatic crystal field splitting with the quantization axis *z* , directed along the *c* axis of the crystal. This is indicated, among other things, by the line shift data we obtained, presented in the next section. Thus, based on our estimates, it can be assumed that the value observed in the experiment ν_Q most likely arises as a result of the predominance of the lattice contribution over the valence contribution $\nu_Q = {}^{51}\nu_Q^c - {}^{51}\nu_Q^v$, with a value of ${}^{51}\nu_Q^v \approx 0.46$ МГц , and the transition of VSe$_2$ to the CDW state is accompanied by a decrease in the valence contribution to the EFG (Fig. 6). Based on this, the difference in the population of 3 *d* - orbitals of vanadium ions can be obtained:

$$ \left(n_{x^2-y^2} + n_{xy}\right) - \left(n_{z^2} + \frac{1}{2}n_{xz} + \frac{1}{2}n_{yz}\right) = \\ = \frac{{}^{51}\nu_Q^v}{{}^{51}\nu_{3d}^v(1-R)}. \quad (4) $$

Taking into account the possible values of the valence contribution screening coefficient $|R| \leq 0.2$ [29], the population difference in expression (4) can take values from 0.25 to 0.39. At the same time, the change in the valence contribution (Fig. 6) indicates a redistribution of electron density during the transition to the CDW state.

The insert of Fig. 6 shows the temperature dependences of the line broadening for the central transition and the first pair of satellites. The figure shows that at the temperature corresponding to the transition to the CDW state, both lines experience broadening. As already noted, charge inhomogeneities in the first order of perturbation theory cannot affect the width of the central transition line. The broadening of the central transition line is associated with the appearance of a distribution of local magnetic field throughout the crystal during the transition to the CDW state. The cause of additional local magnetic fields could be changes in spin densities near the probe nucleus.

Charge and spin degrees of freedom in the crystal are naturally connected, as they are characteristics of a unified electronic system. Information about the spatial distribution of spin densities in the VSe$_2$ crystal can be obtained from the analysis of NMR line shifts of ^{51}V.

SPIN DISTRIBUTION

In Fig. 4, it can be seen that the NMR spectral line of ^{51}V, in addition to the changes described above when approaching temperatures corresponding to the sample's transition to the CDW state, shifts to higher frequencies. At the lowest temperatures ($T < 40$ K), the peak corresponding to the central transition in the spectrum shifts to the frequency region with a value of $K > 0$. When analyzing NMR line shifts in polycrystalline samples, the components of the magnetic shift tensor in the principal axes of the EFG tensor are most often used, represented as K_{iso}, K_{ax}, K_{ani} – isotropic, axial, and anisotropic respectively, which are related to the Cartesian components by known expressions [39]:

$$ \mathrm{K_{iso}} = \frac{1}{3}\left(\mathrm{K_{zz}} + \mathrm{K_{xx}} + \mathrm{K_{yy}}\right), \quad (5) $$

$$\mathrm{K_{ax}} = \frac{1}{3}\left(\mathrm{K_{zz}} - \frac{1}{2}\left(\mathrm{K_{xx}} + \mathrm{K_{yy}}\right)\right),$$

$$K_{\text{ani}} = \frac{1}{2}(K_{xx} - K_{yy}).$$

Fig. 7 shows the temperature dependence of the line shifts K_{iso}, K_{ax}, obtained from the analysis of the spectra in Fig. 4. The value of K_{ani} remained equal to zero when processing each of the spectra.

Fig. 7. Temperature dependences of the isotropic K_{iso} and axial K_{ax} components of the magnetic shift tensor of the NMR line of ^{51}V.

Fig. 8. Dependencies of isotropic K_{iso} and axial K_{ax} components of the magnetic shift tensor of NMR ^{51}V line on magnetic susceptibility ⍰$_0$ in VSe$_2$ with CDW. Straight lines are the result of data approximation.

From the figure, it can be seen that the line shift has negative isotropic and positive axial components at temperatures above the transition temperature T_0. The figure also shows that the behavior of shifts repeats the behavior of magnetic susceptibility $\chi_0(T)$, presented in Fig. 2 and obtained by subtracting the contribution corresponding to the Curie-Weiss law from the experimental data. The absence of sharp changes in the line shift below 25 K is additional evidence that the sharp increase in magnetic susceptibility in the low-temperature region (Fig. 2) may be associated with paramagnetic impurities in low concentration, which could be self-intercalation defects from vanadium atoms. The proportionality of shifts and magnetic susceptibility is confirmed by linear dependencies $K_{\text{iso}}(\chi_0)$, $K_{\text{ax}}(\chi_0)$ presented in Fig. 8. The magnetic susceptibility (Fig. 2), after accounting for the paramagnetic contribution of defects, will be determined by two main contributions: Pauli spin susceptibility of conduction electrons (χ_s) and orbital susceptibility of d-electrons χ_{orb}.

$$\chi_0 = \chi_s + \chi_{\text{orb}}. \qquad (6)$$

The only term in (6) that will depend on temperature is the spin susceptibility χ_s, which is, to a first approximation, proportional to the density of states at the Fermi level $N(E_F)$. The observed decrease in χ_0 (Fig. 2) below T_0 is associated with a decrease in $N(E_F)$ during the phase transition to the CDW state [29] .

The magnetic shift of the NMR line on ^{51}V $K(T)$ nuclei in VSe$_2$ can be written as two contributions:

$$\mathrm{K} = \mathrm{K_s} + \mathrm{K_{orb}} = \\ = \frac{1}{N_A \mu_B}\left(H_{\text{hf,s}}\chi_s + H_{\text{hf,orb}}\chi_{\text{orb}}\right), \qquad (7)$$

where N_A is Avogadro's number. The first term in expression $K_s \sim H_{\text{hf,s}}\chi_s$ represents the spin contribution to the shift from conduction electrons with hyperfine field (HFF) at the nucleus $\mathrm{H_{hf,s}}$, normalized to the Bohr magneton (μ_B) . The second term is the orbital contribution to the shift ($\mathrm{K_{orb}}$), which is predominantly independent of temperature and electron population at the Fermi level [40]. Thus, the changes in the line shift $K(T)$ observed in Fig. 7 are associated with changes in the spin magnetic susceptibility ⍰$_s$ of the vanadium ion electrons, arising from the decrease in $N(E_F)$ during the sample transition to the CDW state. The presence of such changes allows obtaining the value of $\mathrm{H_{hf,s}}$ from the slope of the line in the parametric dependence $K(\chi_0)$.

Since the shift contains isotropic and axial components, it is possible to determine the corresponding contributions to the HFS separately:

$$\begin{gathered}\mathrm{H_{hf}^{iso}} = 74(4)\ \text{кЭ}/\mu_\mathrm{B},\\ \mathrm{H_{hf}^{ax}} = -10(1)\ \text{кЭ}/\mu_\mathrm{B}.\end{gathered} \tag{8}$$

As noted above, the V $^{+4}$ ion has one valence electron, which, in general, can be in the 4 *s or* 3 *d state.* The value $\mathrm{H_{hf}^{iso}}$ obtained in expression (8) can be represented as the sum of two possible isotropic contributions:

$$\mathrm{H_{hf}^{iso}} = \mathrm{H_c} + \mathrm{H_{cp}}. \tag{9}$$

The first term $\mathrm{H_c}$ is the Fermi contact field, resulting from spin polarization on the 4 *s* -orbital and non-zero probability of detecting an electron at the nucleus. This interaction has a positive hyperfine interaction (HFI) constant and the following value for one 4 s - electron of the V ion: $\mathrm{A_c^{4s}} = 3.55\ \text{МЭ}/\mu_\mathrm{B}$ [36]. The second term $\mathrm{H_{cp}}$ is the ionic core polarization field, arising from the interaction of the spin on the outer 3 *d* -orbital with the inner filled *s* -orbitals of the ion. It has a negative HFI constant $\mathrm{A_{cp}^{3d}}$, and can take values up to $-125\ \text{кЭ}/\mu_\mathrm{B}$ [41]. It should be noted that the presented values refer to the case when electrons with spin parallel to the external magnetic field $\mathrm{n}\uparrow$ outnumber electrons with spins in the antiparallel state $\mathrm{n}\downarrow$:

$$\mathrm{H_{hf}^{iso}} = (\mathrm{n}\uparrow - \mathrm{n}\downarrow)\mathrm{A^{iso}}. \tag{10}$$

Since the magnetic spin moments for electrons near the upper boundary of the Fermi distribution are predominantly in a state parallel to the external magnetic field $(\mathrm{n}\downarrow < \mathrm{n}\uparrow)$, and our obtained value $\mathrm{H_{hf}^{iso}} < 0$, we can conclude about the predominant contribution of $\mathrm{H_{cp}}$ in expression (9), with the difference in spin population ($\mathrm{n}^{\uparrow} = \mathrm{n}\uparrow - \mathrm{n}\downarrow$) on the 4 *s* -orbitals of the V $^{+4}$ ion not exceeding 2%.

Fig. 9. Dependencies of components $K_{xx,yy,zz}$ of the axial contribution. Straight lines – result of data approximation.

For a detailed analysis of the obtained value $\mathrm{H_{hf}^{ax}}$, we constructed, using system (5), the dependencies of the shift tensor components on susceptibility in Cartesian coordinates, presented in Fig. 9.

From the figure, it can be seen that the axial shift of the NMR line ^{51}V leads to the emergence of a negative component K_{zz} and positive components K_{xx} and K_{yy} . Similar behavior of the line shift was also observed in the study of a single-crystal sample [17]. In this case, the value of the hyperfine field $\mathrm{H_{hf}^{zz}}$ is negative, and $\mathrm{H_{hf}^{xx,yy}} \approx -\frac{1}{2}\mathrm{H_{hf}^{zz}}$. Such a shift tensor indicates the dipolar nature of the anisotropic hyperfine field. We calculated the dipolar field induced on the ^{51}V nuclei from neighboring ions in the $\mathrm{VSe_2}$ -structure. The maximum value of such a dipolar field corresponds to the direction along the *c* axis of the crystal, against the polarization of the spin moments, and is $\mathrm{H_{dip}^{zz}} = -1.5\ \text{кЭ}/\mu_\mathrm{B}$, which is insufficient to describe the experimental data. The cause of additional dipolar fields may be the spin polarization of 3 *d* -electrons of the vanadium ion [37].

The dipolar field created by one electron on the 3 dz^2 -orbital with a magnetic spin moment directed along the quantization axis *z* ($\mathrm{n}\uparrow$) is determined by the expression [37]:

$$\mathrm{A_{sd}^{3d}} = \frac{4}{7}\mu_\mathrm{B}\, g\langle r^{-3}\rangle = 262\ \text{кЭ}/\mu_\mathrm{B}, \tag{11}$$

where g is the Landé factor.

Considering that the magnetic spin moments on the vanadium ion orbitals are directed along the field, and the EFG on the ^{51}V nuclei is formed predominantly by positive charges, the obtained values allow estimating the difference in spin densities on the 3 *d* - orbitals of the vanadium ion:

$$\left(\mathrm{n}^{\uparrow}_{z^2} + \frac{1}{2}\mathrm{n}^{\uparrow}_{xz} + \frac{1}{2}\mathrm{n}^{\uparrow}_{yz}\right) - \left(\mathrm{n}^{\uparrow}_{x^2-y^2} + \mathrm{n}^{\uparrow}_{xy}\right) = \frac{\left|\mathrm{H}^{zz}_{\mathrm{hf}}\text{-}\mathrm{H}^{zz}_{\mathrm{dip}}\right|}{\mathrm{A}^{3d}_{\mathrm{sd}}} = 0.074\,. \tag{12}$$

To determine the energy of spin-polarized electrons, we constructed the function presented in expression (12), where we used the values of spin densities for each *d* - orbital, calculated from first principles in work [10] (Fig. 10).

Fig. 10. The upper part of the figure shows the function from expression (12). The lower part shows the density of states of 3 *d* - electrons of the vanadium ion, calculated in work [10]. Dashed lines indicate the energies $\mathrm{E}-\mathrm{E}_{\mathrm{F}}$, corresponding to the obtained estimates of the HFI.

From the figure, it can be seen that the obtained estimates of the HFI are possible at two different energy values $\mathrm{E}-\mathrm{E}_{\mathrm{F}}$, each of which is below the Fermi level.

NMR shift values provide information about the spatial distribution of spin densities in the crystal. Figure 6 shows that the central transition line experiences slight inhomogeneous broadening. Similar broadening was also observed in single crystal spectra [17]. We were able to obtain inhomogeneous broadening that satisfactorily describes the experimental spectra by introducing additional local magnetic fields ΔH_x, ΔH_y, ΔH_z, distributed along the principal axes of the EFG tensor with deviations of 75 Oe, 75 Oe, and 150 Oe respectively.

Recent studies of monolayer VSe_2 samples [22-24] established the commensurability of the CDW with the crystal lattice period in the plane and the presence of ferromagnetism [8, 9]. It is not possible to obtain more detailed information about the crystallographic directions of CDW development and their relationship in adjacent planes and their domain structure from NMR data on polycrystalline samples. However, the data obtained in this work, the estimates and conclusions presented on their basis, may prove useful in further NMR studies of single crystal and thin samples of dichalcogenides.

CONCLUSION

For the first time, a systematic NMR study of a polycrystalline VSe_2 sample has been performed. NMR spectra of ^{51}V were obtained and processed over a wide temperature range in an external magnetic field H = 92.8 kOe. From the analysis of the spectra, the EFG tensors and magnetic shift were determined.

The obtained data indicate trigonal-antiprismatic crystal field splitting of the energy levels of 3 *d* - electrons of V ions in 1T-VSe_2 . The reason for such splitting appears to be the pronounced two-dimensional nature of the structure under study. At the same time, data on the local charge environment indicate a close occupancy of the $\mathrm{n}_{x^2-y^2}, \mathrm{n}_{xy}, \mathrm{n}_{z^2}$ 3 *d* -orbitals of the vanadium ion, assuming low occupancy values n_{yz} and n_{xz} , which is in agreement with first-principles calculations [24].

From the analysis of spectra, the change in quadrupole frequency $\Delta\nu_{\mathrm{Q}}$ was determined during the transition to the CDW state, which is a characteristic of charge inhomogeneity in the crystal. The transition to the CDW state is most likely accompanied by a decrease in the valence contribution, which is associated with a decrease in the number of electrons at the Fermi level $N(E_{\mathrm{F}})$ and redistribution of electron density. The difference in spin densities obtained by us indicates a higher spin density of $\mathrm{n}^{\uparrow}_{z^2}$ electrons compared to $\mathrm{n}^{\uparrow}_{x^2-y^2}$, $\mathrm{n}^{\uparrow}_{xy}$, which is apparently related to changes in the energy of these states in an external magnetic field [23, 24].

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CONFLICT OF INTERESTS

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

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