MAGNETIC STATE OF VANADIUM IN CHALCOGENIDE V_7Se_8

© 2025 N. A. Utkin[a,b], M. E. Kashnikova[a,b], Yu. V. Piskunov[a,*], A. G. Smolnikov[a], V. V. Ogloblichev[a], A. F. Sadykov[a], A. P. Gerashenko[a], N. V. Selezneva[b], and N. V. Baranov[a,b]

[a]Mikheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, Ekaterinburg, Russia
[b]Ural Federal University named after the First President of Russia B. N. Yeltsin, Ekaterinburg, Russia

**e-mail: piskunov@imp.uran.ru*

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Abstract. The structural and magnetic properties of V_7Se_8 chalcogenide were studied using X-ray diffractometry, magnetic susceptibility measurements and nuclear magnetic resonance (NMR) spectroscopy on ^{51}V nuclei. The ordering of vacancies in vanadium cationic layers with the formation of a 4*C*-type superstructure was found. It is estimated that the effective magnetic moment of vanadium ions is $\mu_{eff} = 0.35\ \mu B$. A significant local charge and magnetic heterogeneity of the V_7Se_8 compound has been revealed. The hyperfine interaction constant in vanadium ions is estimated from the temperature dependences of the magnetic shift of the NMR ^{51}V line and the susceptibility $\chi(T)$ in V_7Se_8. A joint analysis of the NMR line shift data and the spin-lattice relaxation rate of ^{51}V showed that the 3*d*-electrons of vanadium are in a itinerant state. At the same time, with decreasing temperature in the V_7Se_8 system, antiferromagnetic correlations are induced between the magnetic moments of vanadium in adjacent layers.

Keywords: *transition metal chalcogenides, nuclear magnetic resonance, spin-lattice relaxation, hyperfine fields*

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INTRODUCTION

Vanadium chalcogenide V_7Se_8 belongs to the class of cation-deficient layered compounds M_7X_8, where M is a transition metal atom, X is a divalent anion from group VI of the Mendeleev table - S, Se, Te. These compounds are characterized by the presence of vacancies in the cationic layers, as well as the formation of different superstructures as a result of ordering of vacancies and M atoms in the layers. Vacancies in compounds M_7X_8 with NiAs-type structure are distributed in every second basal layer of transition metal atoms, which is the basic principle of formation of these superstructures (see Fig. 1).

Fig. 1. Unit cell of the 4C superstructure of V_7Se_8 compound. The basic unit cell is shown by dotted lines.

Interest in M_7X_8 systems is due to the fact that compounds of this group of chalcogenides Fe_7S_8 and Fe_7Se_8 are ferrimagnets with high Curie temperatures of 588-598 K [1, 2] and 450-483 K [3, 4], respectively. The magnetic moments of iron in these compounds are ordered ferromagnetically within the layers, while the interaction between layers is antiferromagnetic. Due to the presence of vacancies in every second layer, the magnetic moments are not completely compensated, which leads to the existence of a resultant magnetization and ferrimagnetism of these compounds [2, 5]. In attempts to further improve the magnetic properties of Fe_7S_8 and Fe_7Se_8, studies were conducted on the effect of substituting iron with atoms of other 3 *d* -elements: titanium, vanadium, chromium, manganese, cobalt, and nickel.

In the work [6], the effect of substitution of iron in the compound Fe_7Se_8 with 3 to 10 at. % of Ti, V, Cr, Mn, Co, and Ni atoms was studied. It has been shown that the presence of even a small amount of transition metal atoms leads to strong changes in magnetic properties. Thus, when iron is substituted with titanium or vanadium up to 10 at. %, there is a decrease in the effective magnetic moment of iron from 5.8 to 4 μ_B. A similar trend is observed in the behavior of μ_{eff} when substituted with up to 10 at. % of cobalt or nickel atoms. Substitution in the cation sublattice with chromium or manganese atoms has practically no effect on the magnetic state of iron ions. Analysis of experimental data showed that to explain the change in the magnetic state in such systems, one cannot rely on either the model of completely localized moments or the model of collectivized electrons [6].

The reason for the strong concentration dependence of T_C and magnetization in $Fe_{7-x\,x}V_xSe_8$ has not been fully elucidated. It is unclear whether it is related to the collectivization of 3 *d* -electrons of iron ions and/or to the transition of Fe ions from a high-spin to a low-spin state due to changes in the crystal field when lattice parameters change. It also cannot be excluded that vanadium ions, having a small moment, act as a diluent of the iron magnetic subsystem. This exact reason for the decrease in T_C and magnetization when iron is substituted with weakly magnetic cobalt was discovered by us in $Fe_{7-x\,x}Co_xSe_8$ in works [7, 8]. In any case, to determine the magnetic state of vanadium ions, it is necessary to study the composition with complete substitution of iron ions with vanadium.

In this work, we have conducted a study of the structural and magnetic properties of the compound V_7Se_8 by means of X-ray diffraction, NMR of ^{51}V, magnetic susceptibility measurements and utilization.

SAMPLES AND RESEARCH METHODS

The polycrystalline sample of V_7Se_8 was obtained by solid-phase reactions in an evacuated quartz ampoule. Starting materials: vanadium (purity 99.95 %), selenium of "extra pure" grade (purity 99.999 %). The ampoule was slowly heated in a furnace at a rate of about 15°C/hour to a temperature of 800°C with intermediate holdings at 200°C, 400°C, and 600°C for one day at each temperature. Then the sample was annealed at a temperature of 800 °C for 2 weeks. This was followed by three homogenization anneals (each for one week) in an evacuated quartz ampoule at 750°C. Before each annealing, the sample was ground and pressed into a tablet. This method allowed obtaining a homogeneous single-phase material.

Phase composition analysis and crystal structure investigation were carried out using a Bruker D8 Advance X-ray diffractometer with a LynxEye position-sensitive detector (Cu $K\alpha_{1,2}$ -radiation). The experimental and calculated diffraction patterns of the V_7Se_8 compound are presented in Fig. 2. X-ray structural analysis showed that the V_7Se_8 compound has a layered NiAs-type crystal structure, crystallizes in the monoclinic system (space group $F2/m$) with unit cell parameters: $a = 12.463(4)$ Å, $b = 7.079(4)$ Å, $c = 23.900(3)$ Å , $\beta = 90.961(3)°$. It was found that the V_7Se_8 compound has a 4C superstructure $[a_o 2\sqrt{3}\times 2a_o \times 4c_o]$, where a_o and c_o are the parameters of the basic hexagonal NiAs cell.

Fig. 2. Diffraction pattern of the V_7Se_8 compound (space group $F2/m$). Symbols represent observed intensities, solid line represents calculation, bottom shows the difference curve between observed and calculated intensities. Dashes show the position of reflections in the structure described by the space group $F2/m$.

Field and temperature dependences of magnetization of V_7Se_8 were measured using MPMS SQUID XL7 (Quantum Design) in the temperature range from 2 K to 350 K in magnetic fields up to 70 kOe. 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. A silver resonance coil was used to exclude NMR signals from metallic copper. 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, the power of the radio frequency amplifier was $N = 300$ 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 echo signals accumulated in the required frequency range with a step of $\Delta\nu = 100$ kHz. The nuclear spin-lattice relaxation rate T_1^{-1} was measured using the technique of inversion and subsequent recovery of nuclear magnetization.

RESULTS AND DISCUSSION

Temperature dependence of magnetic susceptibility $\chi(T)$ of V_7Se_8 in the temperature range from 2 to 350 K is shown in Fig. 3. The inset shows $\chi(T)$ in the range of $T = 75–350$ K in a different scale for clarity. As can be seen from the figure, the dependence of $\chi(T)$ in the studied chalcogenide is well described by the Curie-Weiss law (solid line in the figure inset):

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

where C is the Curie constant, θ is the paramagnetic Curie temperature. The value $\chi_0 = |_{dia} + |_{P} + |_{orb}$ represents the sum of temperature-independent contributions determined by the diamagnetism of filled electron shells, paramagnetism of free charge carriers (Pauli paramagnetism), and partial unfreezing of orbital moments of 3d-electrons of vanadium. The value $\chi_0 = 5.14 \cdot 10^{-4}$ emu/Oe·mol was found by extrapolating the dependence of | on the inverse temperature $1/T$ to the region $1/T \to 0$, which corresponds to $T \to \infty$ (see inset in Fig. 4). Fig. 4 shows the dependence of $\frac{1}{\chi-\chi_0} = \frac{1}{C}T - \frac{\theta}{C}$ χ-1 on temperature. Approximation of this dependence by a straight line easily allows obtaining the following values: $C = 0.0155$ emu K/Oe·mol, $\theta = -1.5$ K. From $C = \frac{N_A\mu^2_{эфф}}{3k_B}$C we find $\mu_{эфф} = 0.35\ \mu_B$. Close to this value of the effective moment are the values $\mu^{Co}_{эфф} \approx 0.20\ \mu_B$ and $\mu^{Co}_{эфф} \approx 0.36\ \mu_B$ previously obtained by us for cobalt ions in compounds Co_7Se_8 and $Fe_4Co_3Se_8$ respectively [7, 8]. As seen from the figure, anomalies in the temperature dependence of susceptibility are observed near temperatures 50 K and 175 K. In [9], anomalies in the behavior of the coefficient of linear thermal expansion and electrical resistivity in the chalcogenide V_7Se_8 were observed at these same temperatures. The author associated these anomalies with possible structural phase transitions in the compound, without specifying, however, the details of these transitions. To accurately and in detail describe the structure of the compounds before and after the transition and to identify the main factors determining the pattern of structural changes, it is necessary to conduct experiments on low-temperature radiography.

Fig. 3. Temperature dependence of magnetic susceptibility $\chi(T)$ in V_7Se_8, measured in an external magnetic field $H = 10$ kOe. The inset shows the $\chi(T)$ dependence in the temperature range $T = 75 – 350$ K. The solid line is the result of fitting the experimental data with the expression $\chi(T) = C/(T - \theta) + \chi_0$.

Fig. 4. Dependence of the value $1/(\chi - \chi_0)$ on temperature. The solid line is an approximation of the data by a straight line. The inset shows the dependence of magnetic susceptibility on the inverse temperature $1/T$.

Fig. 5 demonstrates the field dependence of the magnetization of the V_7Se_8 sample, measured up to $H = 70$ kOe. As we can see, the hysteresis is practically absent; the small spontaneous magnetization is apparently due to the presence of an impurity magnetic phase in the sample, the volume of which does not exceed 1–2%, as it is not detected by X-ray diffraction. Thus, the measurement of the temperature dependence of magnetic susceptibility and the field dependence of magnetization indicate that the main phase of the V_7Se_8 sample in the temperature range from 2 K to 300 K is paramagnetic. To determine the possible spontaneous magnetization in the main V_7Se_8 phase, the Belov-Arrott method was used. The inset of Fig. 5 shows the dependence of the square of magnetization M^2 on the ratio H/M. Extrapolation of the linear high-field section (shown by the line in the figure) of this dependence to $H/M = 0$ leads to a clearly negative value of M^2. This indicates that spontaneous magnetization in zero field in the main phase of V_7Se_8 is absent.

Fig. 5. Field dependence of magnetization of the compound V_7Se_8 at a temperature of 2 K. The inset shows the Belov-Arrott plot. The solid line approximates the high-field linear part of the dependence.

Figure 6 shows the NMR spectrum of ^{51}V nuclei in a polycrystalline sample of V_7Se_8, obtained at $T = 293$ K in an external magnetic field $H_0 = 92.8$ kOe. The nucleus of the ^{51}V isotope has a spin $^{51}I = 7/2$ and an electric quadrupole moment $e\,^{51}Q = -0.051 \cdot 10^{-24}$ cm^2. In the case of crystal lattice symmetry lower than cubic, the NMR spectrum of nuclei with spin $I = 7/2$ consists of a set of $2I = 7$ lines. One of the lines corresponds to the central transition ($m = -1/2 \leftrightarrow +1/2$), and the other 6 to satellite transitions ($m = \pm 3/2 \leftrightarrow \pm 1/2$), ($m = \pm 5/2 \leftrightarrow \pm 3/2$) and ($m = \pm 7/2 \leftrightarrow \pm 5/2$). In the spectrum in Fig. 6, resolved satellite lines are not observed. This is obviously due to significant magnetic broadening of the ^{51}V NMR spectrum, as well as the small value of the quadrupole moment $e\,^{51}Q$. In this work, a special spectrum simulation program "Simul" [10] was used to calculate the shape of NMR lines, which numerically calculates energy levels and transition probabilities based on the diagonalization of matrix elements of the Hamiltonian (quadrupole and Zeeman) of the nuclear system. The program allows determining the components of the magnetic shift K_α ($\alpha = x, y, z$ – principal axes of the electric field gradient (EFG) tensor).

Fig. 6. NMR spectrum of ^{51}V nuclei in a polycrystalline sample of V_7Se_8 in a magnetic field $H_0 = 92.8$ kOe at a temperature of $T = 293$ K and the result of modeling the experimental spectrum with a set of three resonance lines 1-3.

Simulation of spectra ^{51}V in V_7Se_8 showed that the complete experimental NMR spectra can be described by at least three different resonance lines, as shown in Fig. 6. Each such line, which we denoted in order of decreasing integral intensity by numbers 1, 2, 3, is characterized by its own magnetic shift K_α. The inability to describe the experimental spectrum with a single resonance line indicates the presence of crystallographically and magnetically nonequivalent vanadium positions in V_7Se_8. As mentioned earlier, there are vacancies in the vanadium sublattice in the V_7Se_8 system. Their presence can lead to differences in the shifts K_α for individual groups of V ions, which is manifested in the differences in their corresponding resonance lines. Unfortunately, it is not possible to identify lines 1-3 by their intensities without additional research. Nevertheless, the NMR spectrum of ^{51}V in Fig. 6 unambiguously indicates a significant local inhomogeneity, both charge and magnetic, of the chalcogenide V_7Se_8.

When analyzing NMR spectra in polycrystalline samples, it is often convenient to switch from components K_α to isotropic $K_{iso} = 1/3(K_x + K_y + K_z)$, axial $K_{ax} = 1/3(K_z - 1/2(K_x + K_y))$ and anisotropic $K_{\text{aniso}} = 1/2(K_y - K_x)$ parts of the NMR line magnetic shift tensor. Spectrum modeling in the "Simul" program showed that the values of K_{ax} and K_{aniso} for lines 1–3 across the entire temperature range are close to zero, and the temperature evolution of K_{iso} for each of these lines is identical. Therefore, Fig. 7 presents $K_{\text{iso}}(T)$ data only for the most intense line 1. As we can see, with decreasing temperature, the shift $K_{\text{iso}}(T)$ changes according to the Curie-Weiss law, following the temperature dependence of magnetic susceptibility $|(T)$. However, at $T < 90$ K, a discrepancy in the behavior of $K_{\text{iso}}(T)$ and $|(T)$ emerges. Unlike the latter, the shift shows a dome-shaped temperature dependence with a broad maximum in the region of $T = 70$ K.

Fig. 7. Temperature dependence of the magnetic shift of ^{51}V K_{iso} in V_7Se_8; the inset shows the dependence of $K_{\text{iso}}(|)$ with temperature as a parameter, approximated by a straight line.

In general, the isotropic magnetic shift of the NMR line on ^{51}V $K_{\text{iso}}(T)$ nuclei can be written as the sum of three main contributions [11]:

$$K_{\text{iso}}(T) = K_s + K_{\text{orb,iso}} + K_{s,\text{iso}}^{CW}(T) . \quad (2)$$

The first term in expression (2) $K_s = \frac{H_c + H_{cp}}{\mu_B}\chi_s$ represents the contribution from conduction electrons. Here H_c and H_{cp} are isotropic constants of hyperfine interaction (HFI) of Fermi contact and core polarization, respectively. The contact contribution to HFI H_c is due to the hyperfine interaction of nuclear spin with valence s-electrons. It is positive and typically significant in metals. The term H_{cp} describes the hyperfine interaction caused by the polarization of filled d-electrons. This contribution is isotropic and, with rare exceptions, negative [12]. The value s-shells of the ion by unpaired ⍰$_s$ is the temperature-independent Pauli spin susceptibility of conduction electrons. The second contribution to the shift, the orbital K_{orb}, is due to the Van Vleck paramagnetism of valence d-electrons of the ion. It arises due to the partial unfreezing of the orbital moment in an external magnetic field, is temperature-independent, and is positive. The third term in (2) is due to localized magnetic moments (LMM) of d-electrons. LMMs on vanadium ions can give two types of contributions to the resonance line shift of ^{51}V nuclei. The first is the contribution from the intrinsic LMMs of V ions, equal to $K_{s,\text{iso}}^{\text{intr}}(T) = \frac{H_{\text{intr}}}{\mu_B}\chi_s^V(T)$, where H_{intr} is the HFI constant of the vanadium nucleus with its own ion electrons, $\chi_s^V(T)$ is the Curie-Weiss susceptibility of LMMs on V ions. The second contribution is due to the magnetic field induced on vanadium nuclei from LMMs of neighboring V ions. This contribution can be written as: $K_{s,\text{iso}}^{\text{tr}}(T) = \frac{H_{\text{tr}}}{\mu_B}\chi_s^V(T)$, where H_{tr} is the constant of induced HFI with neighboring vanadium ions. It is determined mainly by the degree of overlap of d- and s-orbitals of neighboring transition metal ions. Thus, we can represent the shift $K_{\text{iso}}(T)$ in the form of temperature-dependent and temperature-independent parts:

$$K_{\text{iso}}(T) = \frac{H_{\text{intr}} + H_{\text{tr}}}{\mu_B}\chi_s^V(T) + K_0 . \quad (3)$$

Note that the term localized magnetic moments requires some clarification. We obtained for the effective magnetic moment of the vanadium ion the value $\mu_{\text{эфф}} = 0.35\ \mu_B$. This does not mean that 3 d-electrons of V are completely localized. They are mobile enough to hop many times from one lattice site to another during the measurement time. In this case, the intra-atomic exchange interaction polarizes these collectivized electrons (similar to an external magnetic field), leading to the emergence of an uncompensated magnetic moment of the ion. The temperature dependence of the susceptibility of such collectivized electrons is usually close to the Curie-Weiss law [13].

In turn, the magnetic susceptibility $\chi(T)$ also consists of two main contributions: the spin susceptibility that depends on temperature according to the Curie-Weiss law $\chi_s^{\mathrm{V}}(T)$ and temperature-independent contribution $\chi_0 = \chi_s + \chi_{\mathrm{orb}}$:

$$\chi(T) = \chi_s^{\mathrm{V}}(T) + \chi_0 . \qquad (4)$$

Using expressions (3) and (4), one can obtain the dependence of the shift K_{iso} on χ with temperature as a parameter:

$$K_{\mathrm{iso}}(\chi) = \frac{H_{\mathrm{intr}}+H_{\mathrm{tr}}}{\mu_{\mathrm{B}}}\chi(T) - \frac{H_{\mathrm{intr}}+H_{\mathrm{tr}}}{\mu_{\mathrm{B}}}\chi_0 + K_0 , \qquad (5)$$

which has the form of a straight line with a tangent of the slope angle equal to $\frac{H_{\mathrm{intr}}+H_{\mathrm{tr}}}{\mu_{\mathrm{B}}}$. Such a parametric dependence $K_{\mathrm{iso}}(\chi)$ is presented in the inset of Fig. 7. By approximating the data of the parametric dependence $K_{\mathrm{iso}}(\chi)$ with a straight line (5), we find the value of the total constant of the intrinsic and induced HFI of vanadium nuclei $H_{\mathrm{intr}} + H_{\mathrm{tr}} = 200(5)$ kOe/ μ_{B}.

It is known that one unpaired electron in the 3 *d* -shell of a transition element creates an isotropic core polarization field on the nucleus $H_{\mathrm{cp}} = -125$ kOe [14], and in the 4 *s* -shell of vanadium – a contact HFI $H_{\mathrm{c}} = 3400$ kOe [15]. In our case, the total value of HFI from collectivized electrons is 200(5) kOe/ μ_{B}. Consequently, we must assume that there is significant 4 *s* -3 *d* -hybridization in vanadium ions, and that spin polarization is transferred between neighboring V ions (through induced HFI H_{tr}) not only through 3 *d* -orbitals, but also through 4 *s* -orbitals.

As can be seen from Fig. 3 and Fig. 7, the shift $K_{\mathrm{iso}}(T)$ and susceptibility $\chi(T)$ behave differently below $T = 90$ K. The former demonstrates a maximum near $T = 70$ K, while $\chi(T)$ has a Curie-Weiss dependence down to $T = 2$ K. This difference may be caused by the following reasons. First, the presence of short-range antiferromagnetic (AF) correlations. As already mentioned in the introduction, in the $\mathrm{Fe_7Se_8}$ magnet, which has the same NiAs-type structure as $\mathrm{V_7Se_8}$, the magnetic moments of iron order ferromagnetically within each layer, but antiferromagnetically with respect to the two adjacent layers. That is, there are strong AF correlations between the layers. In the presence of such correlations in the paramagnetic state of the $\mathrm{V_7Se_8}$ chalcogenide, mutual compensation of in-plane and interplane contributions to the induced HFI H_{tr} may occur. As a result, this field, and consequently the value of $K_{\mathrm{iso}}(T)$, will decrease with decreasing temperature. We have previously observed a similar effect in the $\mathrm{Fe_4Co_3Se_8}$ chalcogenide [8]. It would seem that with the presence of AF correlations, the magnetic susceptibility should also deviate from Curie-Weiss behavior. But this is not observed. The fact is that the NMR magnetic shift is proportional to the *homogeneous* contribution to the spin susceptibility $\chi(q = 0)$. The molar susceptibility $\chi(T)$ may include *inhomogeneous* terms across the sample. These include contributions from various types of impurities, as well as magnetic or non-magnetic clusters distributed within the studied sample. Apparently, we are dealing with such microinhomogeneities in the $\mathrm{V_7Se_8}$ sample. They make a significant contribution to $\chi(T)$, especially at low temperatures, but not to the NMR line shift.

Results of measurements of the spin-lattice relaxation (SLR) rate T_1^{-1} of nuclear magnetization $M_z = {}^{51}\gamma_{\mathrm{n}} \hbar < I_z(t) >$ of vanadium ions in the compound $\mathrm{V_7Se_8}$ are presented in Fig. 8. Spin-lattice relaxation of macroscopic nuclear magnetization $M_z(t)$ to thermodynamic equilibrium value M_0 occurs over a characteristic time T_1.

In the free electron gas approximation in metals, the value of T_1^{-1} increases proportionally to temperature. In this case, the so-called Korringa relation [16] is satisfied:

$$\left(\frac{1}{T_1}\right)_K = \left(\frac{\gamma_n}{\gamma_{\mathrm{e}}}\right)^2 \frac{4\pi k_B}{\hbar} K_s^2 T , \quad (6)$$

where γ_e and γ_n are the electronic and nuclear gyromagnetic ratios. This relation is a consequence of the fact that relaxation and shift in a metal are determined respectively by the fluctuating and static parts of the local magnetic field caused by the hyperfine interaction of nuclei with conduction electrons. In addition, in 3 *d* -metals, the so-called orbital contribution to SLR $\left(\frac{1}{T_1}\right)_{\text{орб}}$ can be significant, caused by fluctuations of orbital currents of *d* -electrons. Unlike the orbital contribution to the magnetic shift, the term $\left(\frac{1}{T_1}\right)_{\text{орб}}$ is not related to the orbital susceptibility χ_{orb} and therefore cannot be expressed through the shift $K_{\text{orb.}}$ This contribution is determined directly by the density of *d* electronic states at the Fermi level and, like $\left(\frac{1}{T_1}\right)_K$, is proportional to temperature [17]. Thus, in 3 *d* -metals, the temperature dependence of the SLR rate may have a Korringa type, i.e., $1/T_1 \propto T$. Fluctuations of local magnetic moments can also lead to nuclear spin-lattice relaxation. This contribution in the paramagnetic region is temperature-independent, $\left(\frac{1}{T_1}\right)_{\text{lmm}} = \text{const}$ [18].

Fig. 8. Temperature dependence of the nuclear spin-lattice relaxation rate T_1^{-1}Dashed line – approximation of data at $T \geq 90$ K by a straight line.

Fig. 8 demonstrates that in V_7Se_8 in the temperature range of 300-90 K, the spin-lattice relaxation (SLR) rate $T_1^{-1}(T)$ of vanadium nuclear moments is proportional to temperature, i.e., it has a Korringa-like character, which is additional confirmation that this compound, at least in this temperature range, is a Pauli paramagnetic metal. Furthermore, extrapolation of the dependence $T_1^{-1}(T)$ to the low-temperature region leads, within the error margin, to a zero value of the SLR rate. This indicates the absence of a contribution from local magnetic moments and that the SLR of vanadium nuclear magnetic moments is determined mainly by conduction electrons.

Below 90 K, the temperature dependence of the SLR rate acquires a nonlinear dome-shaped form. Such temperature dependence is characteristic of systems with AF short-range order. In this case, the peak in $T_1^{-1}(T)$ occurs at a temperature at which a maximum appears in the spectrum of antiferromagnetically correlated fluctuations at the NMR frequency. Thus, the results of measuring the SLR of vanadium nuclear moments also indicate that below $T = 90$ K in the chalcogenide V_7Se_8, short-range AF order is formed; however, long-range magnetic order does not occur down to the lowest temperatures.

CONCLUSION

An investigation of the structural and magnetic properties of the compound V_7Se_8 was performed using X-ray diffraction, magnetization measurements, and nuclear magnetic resonance of ^{51}V nuclei.

X-ray structural analysis showed that the compound V_7Se_8 has a superstructure $4C\,[a_o 2\sqrt{3} \times 2a_o \times 4c_o]$, where a_o and c_o are the parameters of the basic hexagonal NiAs cell.

It was found that the temperature dependence of magnetic susceptibility $\chi(T)$ has anomalies in the temperature range of $T = 175$ K and $T = 50$ K, which indicate possible structural phase transitions in V_7Se_8 at these temperatures. Determining the type of these transitions requires additional research. From the temperature dependence of susceptibility, the value of the effective magnetic moment of vanadium ions was determined as $\mu_{\text{eff}} = 0.35\ \mu_B$. Such a small moment value indicates that the 3 *d* -electrons of vanadium are collectivized.

Analysis of NMR spectra of ^{51}V revealed significant local inhomogeneity, both charge and magnetic, in the compound V_7Se_8. From the temperature dependences of shift and susceptibility in V_7Se_8, an estimate was made of the constant of total, intrinsic and induced hyperfine interaction

$H_{\mathrm{intr}} + H_{\mathrm{tr}}$ = 200(5) kOe/ μ_B of nuclear and electronic magnetic moments of vanadium. A dome-shaped temperature dependence of the NMR line magnetic shift of ^{51}V was discovered at temperatures below 90 K. Such shift behavior indicates the emergence of strong antiferromagnetic correlations between vanadium magnetic moments in adjacent layers at low temperatures.

The small value of μ_{eff} of vanadium ions is also indirectly evidenced by data on the temperature dependence of the spin-lattice relaxation rate of nuclear moments ^{51}V, which demonstrates Korringa-like behavior and the absence of contribution from localized magnetic moments of vanadium ions at $T \geq \geq 90$ K. The deviation from the Korringa temperature dependence of the SLR rate below 90 K indicates the presence of strong AF correlations in the spin fluctuation spectrum of the chalcogenide V_7Se_8.

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CONFLICT OF INTERESTS

The authors declare that they have no conflict of interest.

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