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# Electrical and magnetic properties of intercalated compounds in the $Gd_xNbSe_2$ system ($0 \leq x \leq 0.33$)

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The electrical and magnetic properties were measured on polycrystalline samples of niobium diselenide intercalated with gadolinium atoms. The dependences of the electrical resistance on temperature point to a predominantly phonon scattering mechanism for charge carriers, while the concentration dependences are determined by increasing scattering by interstitial atoms. The magnetic properties of $Gd_xNbSe_2$ ($0 \leq x \leq 0.33$) were studied in the temperature range of 2−350 K and in the range of magnetic fields up to 70 kOe. Based on the results of studies of magnetic susceptibility and magnetization, the possibility of the existence of antiferromagnetic interactions in the studied compounds and the phenomenon of spin reorientation in a magnetic field are shown. The observed decrease in the effective magnetic moment of gadolinium ions with an increase with their concentration is discussed in terms of a possible intramolecular exchange.

**Keywords:** niobium diselenide, gadolinium, intercalation, electrical resistance, magnetization, effective magnetic moment.

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## 1. Introduction

Intercalated compounds based on transition metal dichalcogenides ($T$) with $TX_2$-type ($X$ — chalcogen) laminated atomic structure (LTMD) are one of the types of low-size systems that have been of increasing interest in recent years [1]. Many of them have a wide range of attractive properties such as, for example, niobium diselenide where superconductivity at $T = 7$ K and structural transition with charge-density wave (CDW) at $T = 34$ K [2,3] are observed.

Previous investigations have shown that the physical properties of compounds produced by means of intercalation with 3$d$-element atoms differ from the properties of initial $TX_2$ compounds. Additional interactions of the interstitial atoms with matrix atoms lead to the crystal lattice deformation, changes in the electrical properties of intercalated materials and formation of various magnetic states. Thus, for example, LTMD intercalation with 3$d$-element atoms generally causes suppression of transition into CDW state. Ions of these elements have significantly lower effective magnetic moments as a result of partial hybridization of 3$d$-electrons with electronic states of the matrix intercalated with them [4]. However, there are significantly fewer papers devoted to investigation of LTMDs intercalated with rare earth element atoms (REE). A part of research in this area is devoted to the investigation of misfit layered compounds where REE atoms are contained in a separate structural fragment, and of direct intercalation of mixed-valent REEs [5,6].

REE was chosen as an intercalant because REE-ions have higher magnetic moments. Among them, gadolinium in $Gd^{3+}$ state is characterized by half-occupancy of 4$f$-shell and its magnetic moment is defined only by spin contribution. In $Gd_xTiSe_2$ system thanks to localization of 4$f$-electrons, the effective magnetic moment of the gadolinium ions was complied with the spin values (7.94 $\mu$B), and the magnetic susceptibility temperature dependence within 15−350 K followed the Curie−Weiss law. At low temperatures, abnormalities were detected in $\chi(T)$ dependences and together with negative Curie paramagnetic temperatures were indicative of the antiferromagnetic state below $T = 9$ K [7]. This was also demonstrated by the type of field magnetization dependences of $Gd_xTiSe_2$.

When analyzing physical property generation mechanisms for intercalated compounds, not only the differences in the nature and electronic structure of introduced atoms, but typical features of the initial dichalcogenides used for intercalation shall be addressed. This may be related to dichalcogenides based on V group elements. In particular, niobium diselenide as opposed to $TiSe_2$ may exist in various structural modifications (polytypes). 2$H$-$NbSe_2$ and 4$H$-$NbSe_2$ are the most widespread structures. These structures are characterized by the number of layers in a lattice cell and by the lattice cell parameters accordingly. In addition, as opposed to compounds based on titanium and vanadium dichalcogenides where metal atoms occupy octahedral positions, metal atoms in 2$H$-$NbSe_2$ are arranged in trigonal-prismatic coordination [8]. The second difference is in that one uncompensated electron is remained in niobium 4$d$-shell when $NbSe_2$ is formed, therefore properties of the matrix itself shall be considered.

The paper discusses the investigation of electrical and magnetic properties of synthesized $Gd_xNbSe_2$ samples

carried out in order to study the influence of the crystalline and electronic matrix structure on the physical properties of compounds intercalated with REE -elements.

## 2. Experiment

Polycristalline $Gd_xNbSe_2$ $(0 \le x \le 0.33)$ samples were prepared by solid-state reaction method in evacuated quartz vials [4,7]. The synthesis and further homogenization annealing temperatures (650−700°C) corresponded to the conditions of formation of $NbSe_2$ 2*H*-modification. To qualify the prepared samples, X-ray and microprobe analysis methods were used and diffraction patterns were processed using an application software package. Resistance was measured in the temperature range from 6K*to*320 K using CryoFree204 self-contained closed-cycle cryostat. Magnetic properties were measured using MPMS-XL-7 SQUID magnetometer in the temperature range from 2 K to 350 K and magnetic field range up to 70 kOe.

## 3. Results

Temperature dependences of resistance $\rho$ of $Gd_xNbSe_2$ samples shown in Fig. 1 demonstrate linear growth with temperature increase which is mainly indicative of phonon type of carrier scattering. Increased content of intercalated atoms also results in resistance growth which is associated with increased scattering intensity in structural defects and impurities whose function is performed by introduced gadolinium ions. Such dependence is similar to that found previously in $Cd_xTiSe_2$ system [7]. In low temperature range at $T \to 0$ K, $\rho$ tends to some constant value $\rho_0$ which may be associated with residual resistance due to scattering in impurities and which is increased with gadolinium atom content growth from $0.57\,\mu\Omega \cdot$ m at $x = 0.1$ to $2.95\,\mu\Omega \cdot$ m at $x = 0.33$.

Measurements of magnetic susceptibility $\chi$ of intercalated $Gd_xNbSe_2$ compounds have shown that susceptibility is increased with the gadolinium content in the samples (Fig. 2). The temperature dependences $\chi(T)$ correspond to the paramagnetic state and match well with the Curie−Weiss law as follows:

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

where $\chi_0$ is the temperature-independent term, $C$ is the Curie−Weiss constant, $\Theta_p$ is the Curie temperature.

The results obtained by approximation of the dependence $\chi(T)$ according to (1) are shown in the Table. The fourth and fifth columns contain the effective magnetic moments per formula unit of each compound and per gadolinium ion. Fig. 3 shows the temperature dependences of inverse susceptibility attributed to the Curie−Weiss contribution (the second summand in equation (1)) that have a linear character which proves the reliability of the approximation. The obtained temperature dependences $\chi$ had no any

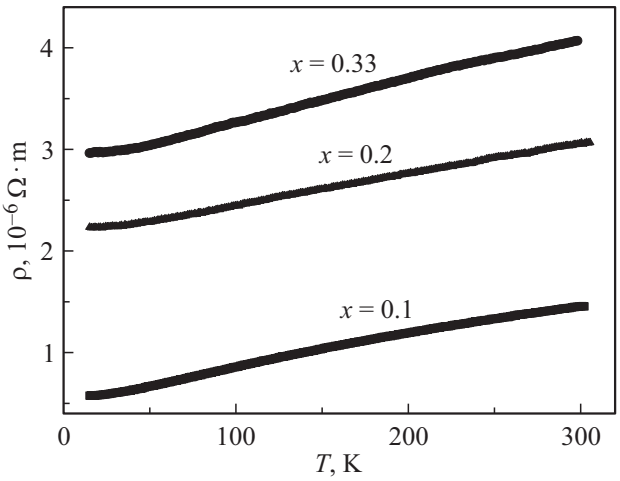


**Figure 1.** Temperature dependences of $Gd_xNbSe_2$ resistance.

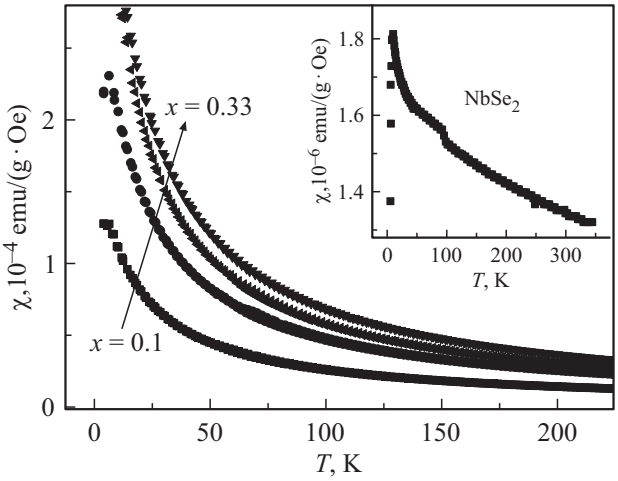


**Figure 2.** Temperature dependences of magnetic susceptibility of $NbSe_2$ (detail) and intercalated $Gd_xNbSe_2$ compounds.

abnormalities in the temperature range corresponding to the Curie temperature for pure gadolinium (approximately 290 K), which may serve as demonstration of completion of the intercalation process.

As previously noted, $Nb^{4+}$ ion in diselenide has one remaining unpaired 4*d*-electron and, thus, $NbSe_2$ matrix may have magnetic moment. Magnetic properties of $NbSe_2$ have been investigated earlier in several papers [3,9], however, no unambiguous idea of the magnetic state of this compound has been get. Detail in Fig. 2 shows the obtained dependence $\chi(T)$ for the initial niobium diselenide. Sudden reduction of $\chi$ at $T < 8$ K corresponds to niobium diselenide transition into a superconductive state. There were attempts to represent $\chi(T)$ for $NbSe_2$ as a sum of several segments with different effective magnetic moments [10]. However, we believe that it is possible to approximate successfully the obtained dependence in a wide temperature range using equation (1) and to define the values of $\theta_p$ for $NbSe_2$ and of effective magnetic moment

Temperature-independent contribution into magnetic susceptibility $\chi_0$, Curie paramegnetic temperature $\Theta_p$, effective magnetic moment per formula unit ($\mu_{\text{eff}}^{fu}$) and per gadolinium ion ($\mu_{\text{eff}}^{\text{Gd}}$)

| $x$ | $\chi_0$, $10^{-6}$ emu/g · Oe | $\Theta_p$, K | $\mu_{\text{eff}}^{fu}$, $\mu_B$ using equation (1) | $\mu_{\text{eff}}^{\text{Gd}}$, $\mu_B$ using equation (1) | $\mu_{\text{eff}}^{\text{Gd}}$, $\mu_B$ using equation (2) |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| 0 | 1.05 | −100 | 0.56 | – | – |
| 0.1 | 0.46 | −17 | 2.54 | 8.02 | 7.84 |
| 0.2 | 1.6 | −21 | 3.55 | 7.94 | 7.84 |
| 0.25 | 1.4 | −19 | 3.88 | 7.76 | 7.68 |
| 0.33 | 2.3 | −16 | 4.36 | 7.54 | 7.52 |

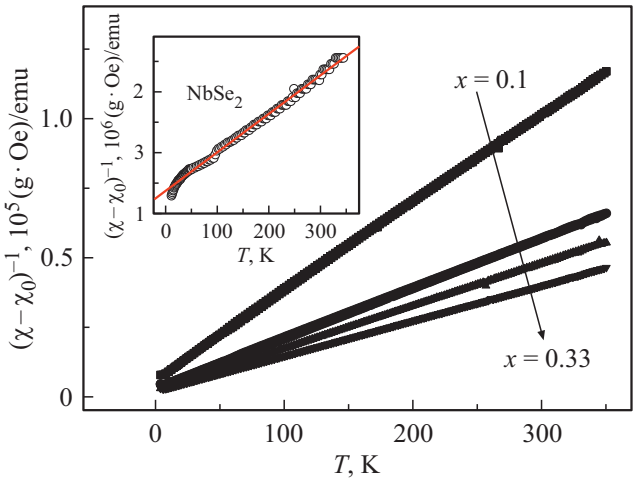


**Figure 3.** Temperature dependences of inverse susceptibility of $NbSe_2$ (detail) and intercalated $Gd_xNbSe_2$ compounds.

of $NbSe_2$ formula unit. Linear dependences of $(\chi - \chi_0)^{-1}$ on temperature shown in the detail in Fig. 3 prove the possibility of such approximation.

The given data shows that the effective magnetic moment per formula unit of intercalated compounds is continuously growing with the gadolinium content and the magnetic moment of gadolinium ion has a downward trend. When considering a possible contribution into magnetic susceptibility of the matrix itself, the effective magnetic moment of gadolinium was also defined using the following equation

$$(\mu_{\text{eff}}^{fu})^2 = (\mu_{\text{eff}}^{\text{NbSe}_2})^2 + x(\mu_{\text{eff}}^{\text{Gd}})^2. \quad (2)$$

For the effective magnetic moment of $NbSe_2$, the value of $0.56\mu_B$ defined by us has been assumed here.

Values of $\mu_{\text{eff}}$ defined for gadolinium ions using this equation are listed in the sixth column of the table. When analyzing the data listed in the table, the absence of clear concentration dependence of the Curie temperature shall be noted, however, its negative values suggest that antiferromagnetic type interactions exist in the studied compounds, including also niobium diselenide. Additional proof may be obtained by means of the analysis of temperature dependences of effective magnetic moments of both gadolinium ions and niobium diselenide. Such calculations were carried out in accordance with the following equation

$$\mu_{\text{eff}}^2 = 8\chi_{\text{mol}}T/x, \quad (3)$$

where $\chi_{\text{mol}}$ is the molar susceptibility, $T$ is the temperature, $x$ is the gadolinium content in $Gd_xNbSe_2$. Calculations for samples with various composition are shown in Fig. 4. It is shown that with the increase in temperature, $\mu_{\text{eff}}^{\text{Gd}}$ values for each sample are growing and asymptotically tend to some constant values that are reduced with the increase in gadolinium content. Such type of dependences $\mu_{\text{eff}}(T)$ is typical of the systems where antiferromagnetic type interactions between magnetic ions occur when the temperature is decreased as, for example, in $Fe_xHfS_2$ [11]. Similar type of dependence is also given for $NbSe_2$ (Fig. 4), which corresponds to the negative value of $\theta_p$ obtained by approximation using equation (1).

Antiferromagnetic type of interaction is also proved by the field dependences of magnetization $M$ of $Gd_xNbSe_2$ samples measured at $T = 2$ K and shown in Fig. 5. These dependences show the absence of saturation up to the fields

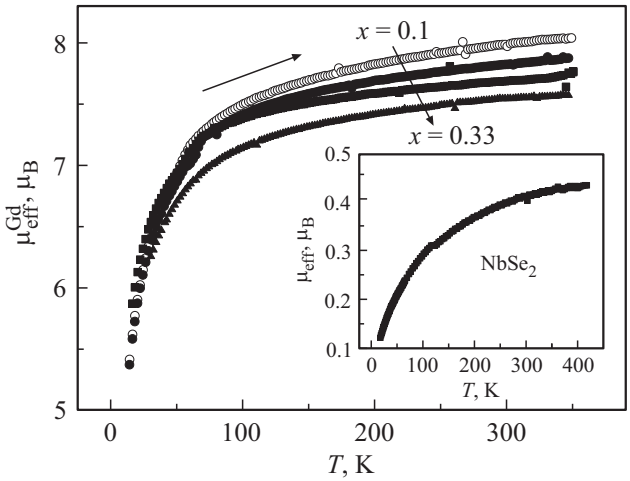


**Figure 4.** Temperature dependence of the effective magnetic moment of $NbSe_2$ (see the detail) and gadolinium ions in $Gd_xNbSe_2$.

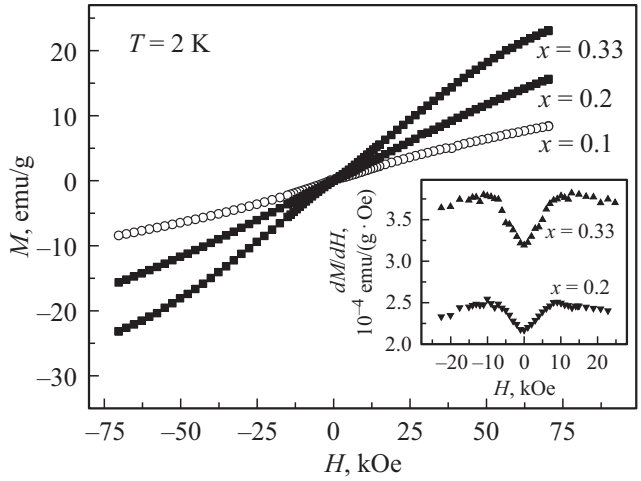


**Figure 5.** Field magnetization dependences of intercalated $Gd_xNbSe_2$ compounds and $dM/dH$ derivatives (see the detail).

with $H = 70$ kOe and have a slight knee associated with spin flip. Critical field $H_r$ equal to approximately 9 kOe was defined by the maximum field dependence $dM/dH$ in Fig. 5. This value is twice as low as the critical field observed in $Gd_xTiSe_2$ system [7,12].

## 4. Conclusion

The investigation of the influence of intercalation with gadolinium atoms on the physical properties of $Gd_xNbSe_2$ compounds carried out herein has shown that temperature dependences of resistance are indicative of the prevailing phonon type of carrier scattering and the increase in resistance with the gadolinium atom concentration is explained by the reduced mobility of carriers when they are scattered over the interstitial atoms. This conclusion is proved by the residual resistance behavior of the samples with various composition.

Increase in the gadolinium content results in the increase in magnetic susceptibility and its temperature dependences for all samples match well with the Curie–Weiss law. As a result of such approximation, values of temperature-independent summand $\chi_0$ and Curie temperature $\theta_p$ were defined. Consideration of the temperature-independent summand made it possible to define the contribution of localized magnetic moments in intercalated compounds. The same approximation was also carried out for niobium diselenide and used to define the effective magnetic moment of the matrix itself which is equal to $0.56\,\mu_B$. The effective magnetic moments of gadolinium ions were defined both by direct approximation of experimental data and by calculation, including the contribution of $NbSe_2$ matrix. In both cases, the findings are indicative of reduced $\mu_{eff}^{Gd}$ as compared with the spin value ($7.94\,\mu_B$). Such reduction was not observed for gadolinium intercalation of titanium diselenide [7]. Since it is scarcely probable that $4f$-electrons of gadolinium can interact with molecular orbitals of the matrix as is the case with intercalation with $3d$-elements, the observed reduction of $\mu_{eff}^{Gd}$ can occur as a result of intramolecular exchange between $4f$-electrons of gadolinium and $4d$-electrons of niobium.

Negative Curie temperature and typical temperature dependence of effective magnetic moments suggest that antiferromagnetic type interactions exist in $NbSe_2$ and $Gd_xNbSe_2$ compounds. However, gadolinium intercalation in $Gd_xNbSe_2$ does not lead to formation of long-range magnetic order or even to spin-glass state with pronounced critical temperatures as were observed before in $Gd_xTiSe_2$ system [7]. This can be explained by means of the analysis of the field magnetization dependences of intercalated compounds which have a knee at the critical field value which is twice as low as in $Gd_xTiSe_2$ system. This demonstrates a significantly lower energy of antiferromagnetic exchange between $4f$-electrons of gadolinium in $Gd_xNbSe_2$. Such differences in magnetic state of the two systems shall be associated with structural and magnetic features of titanium and niobium diselenides used for intercalation.

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### Conflict of interest

The author declares that he has no conflict of interest.

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