Electronic Structure and Hyperfine Interactions in Crx NbSe 2 \((x = 0.33, 0.5)\) by DFT studies

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Electronic Structure and Hyperfine Interactions in Cr$_x$NbSe$_2$ ($x = 0.33, 0.5$) by DFT studies

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Abstract

The first principles calculations of the electronic structure and hyperfine interactions of Cr$_x$NbSe$_2$ ($x = 0.33, 0.55$) chalcogenides are presented. As a result, the values of the hyperfine fields and the parameters of the quadrupole interaction were determined for different arrangements of chromium ions. Ab initio calculations are compared with data obtained by the nuclear magnetic resonance methods on the $^{53}$Cr and $^{93}$Nb nuclei. It has been shown that Cr$^{3+}$ ions have a high degree of hybridization of $a_{1g}$ and $e_g$ orbitals of 3$d$-electrons with 4$d$ and 5$s$ orbitals of niobium. It has been established that two nonequivalent environments of chromium ions coexist in Cr$_{0.33}$NbSe$_2$ compound.

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1 Introduction

The transition metal dichalcogenides $TX_2$ ($T =$ transition metal, $X =$ chalcogen) are among the most studied two-dimensional electronic systems due to their intriguing physical and chemical properties and potential applications.
Moreover, the weak bonding between the $T$–$X$–$T$ sandwiches allows intercalating foreign atoms or molecules in the interlayer space and obtaining materials with new properties that differ significantly from those observed in the parent compounds. Among various intercalate, the 3$d$-transition-metal intercalated $2H$-$NbX_2$ compounds ($X$ = S, Se) are particular interesting. The parent compounds $2H$-$NbS_2$ and $2H$-$NbSe_2$, where $2H$ means two $T$–$X$–$T$ sandwiches in one unit cell, and the compound has a hexagonal symmetry, exhibit metallic type conductivity behavior and transition to the superconducting state below $T = 5.7$ K in sulfide and $T = 7.2$ K in selenide [1]. The intercalation of 3$d$-transition-metal atoms suppresses superconductivity and generates various magnetic states (for example, ferromagnetic or antiferromagnetic), depending on the intercalating species and the host compound [2]–[4].

From these points of view the intercalated compounds $Cr_xNbSe_2$ with $Cr$ concentrations up to $x = 0.5$ were recently studied to reveal the effect of intercalation on the crystal structure, magnetic state, and thermal properties. First of all, it was shown that the selenide compounds $Cr_xNbSe_2$ with $x > 0.33$ demonstrate ferromagnetic ordering [4], [5]. The band-structure calculations and optical spectroscopy studies for $Cr_{0.33}NbSe_2$ have revealed strong hybridization of the $Cr$ 3$d$ and $Nb$ 4$d$ states [6].

The nuclear magnetic resonance (NMR) spectroscopy on various nuclei can provide useful information for a deeper understanding of how the 3$d$-transition metal atoms with a magnetic moment being inserted into $TX_2$ affect the distribution of electron and spin density in the intercalates compounds. Recently [4], [7], such investigations of $Cr_xNbSe_2$ compounds with chromium concentration of $x = 0.33$ and $x = 0.5$ have been performed by means of NMR spectroscopy on $^{53}Cr$ and $^{93}Nb$ nuclei to answer the question about the effect of chromium intercalation on the distribution of spin and charge density in $Cr_xNbSe_2$. Ogloblichev et al [7] paid their attention to reveal how the intercalation of Cr atoms into $NbSe_2$ affects the electron configuration and magnetic state of Nb atoms. As a result, the authors determined the values of hyperfine fields and the parameters of the quadrupole interaction on niobium and chromium nuclei at a temperature $T = 4.2$ K. The presence of a high local magnetic field at the location of niobium nuclei in $Cr_xNbSe_2$ was associated with a high degree of hybridization of the $a_{1g}$ and $4d_{z^2}$ and $5s$ orbitals of niobium.

So, the aims of the present work is to interpret theoretically the experimental NMR data in the framework of the first-principle calculation, estimate the quadrupole interactions of chromium and niobium nuclei in different environments, and determine electronic structure of $Cr_xNbSe_2$ compounds with chromium concentration $x = 0.33$ and $x = 0.5$. 
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2 Details for calculations

First-principles density-functional theory (DFT) calculations were conducted to evaluate the parameters of the NMR and get electronic structure of Cr\(_x\)NbSe\(_2\) compounds. The calculations were carried out using the Vienna Ab initio Simulation Package (VASP) \([8]\) using the projected augmented wave method (PAW) \([9]\) and PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional \([10]\). We adopt the experimental structure parameters \([5]\), then relax the atomic positions of ions to their lowest energy positions. The cut-off energy was taken to be \(E_{\text{cutoff}}=300\) eV and \(8\times8\times4\) Monkhorst-Pack grid of k-points was used during calculations.

3 Results and discussion

3.1 Crystal structures

Intercalation of the parent compound 2H-NbSe\(_2\) with chromium ions leads to the formation of crystal structures with different arrangement of Cr in the lattice.

![Fig. 1](image)

The Cr\(_x\)NbSe\(_2\) compounds with the Cr concentrations \(x < 0.25\) are isostructural to the 2H-NbSe\(_2\) matrix and have a crystal lattice belonging to the space group \(P6_3/mmc\), while ordering of Cr atoms leads to the formation of \(2\times2\) superstructure in Cr\(_{0.25}\)NbSe\(_2\) (see Figure 1). For the concentrations \(0.25 < x < 0.50\), chromium atoms become ordered in the \(ab\) plane with the formation of the \(\sqrt{3} \times \sqrt{3}\) superstructure (space group \(P6_322\), see Figures 2,3). It is important note that in Cr\(_{0.33}\)NbSe\(_2\) the coexistence of regions with orderings of the \(2\times2\) and \(\sqrt{3} \times \sqrt{3}\) type can take place.

The NMR spectroscopy does not allow to directly associated the observed NMR spectrum with a particular space group, but can identify the differences in local symmetry at the positions of resonating nuclei probes. In particular, Ogloblichev et al \([7]\) observed the proximity of the NMR parameters for Cr\(_x\)NbSe\(_2\) with \(x=0.33\) and \(x=0.5\). It indicates that the chromium atoms can
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Fig. 2 The unit cell of $\text{Cr}_x\text{NbSe}_2$ for the $P6_322$-I space group: (a) — a 3D view; (b) — a (010) projection: Cr atoms occupy one third of the octahedral holes in the van der Waals gap; (c) — a (001) projection.

Fig. 3 The unit cell of $\text{Cr}_x\text{NbSe}_2$ for the $P6_322$-II space group: (a) — a 3D view; (b) — a (010) projection: the coexistence of regions with orderings of the $2 \times 2$ and $\sqrt{3} \times \sqrt{3}$ type of Cr atoms takes place; (c) — a (001) projection.

be located in positions with an identical environment despite the different concentrations of the intercalant.

In present work we consider the crystal structures $P6_3/mmc$ (when the ordering of Cr atoms leads to the formation of $\sqrt{3} \times \sqrt{3}$ superstructure;) and $P6_322$ (with two possible orderings of chromium atoms: $P6_322$-I, where the ordering of Cr atoms leads to the formation of $2 \times 2$ superstructure; $P6_322$-II, where the coexistence of regions with orderings of the $2 \times 2$ and $\sqrt{3} \times \sqrt{3}$ type of Cr atoms takes place) to interpret the NMR data [7] and determine the electronic structures for the selenide compounds $\text{Cr}_x\text{NbSe}_2$.

3.2 Electronic structure

First of all, one can note that in the literature the electron structure calculations were performed for $\text{Cr}_{1/3}\text{NbSe}_2$ compound only [6], where the ordering of Cr atoms leads to the formation of $2 \times 2$ superstructure (the $P6_322$-I space group symmetry in our definition). In present work we have performed the calculations of the total (DOS) and partial (pDOS) densities of states for all systems under consideration with different environments of chromium atoms intercalated between NbSe$_2$ layers.
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The Figure 4 shows the total density of states. As can be seen, the profiles of DOS for $P6_3/mmc$ and $P6_322$–I crystal structures are very similar and agree well with those reported previously [6], [11]–[14]. For all systems Se 4$p$ (highlighted by gray) and Nb 4$d$ (highlighted by violet) states are located mainly in the energy intervals $[-7:-2]$ and $[-2:3]$ eV, respectively. Far below the Fermi energy, the total density of states is of Se 4$p$ character. The tail of Se band hybridizes with Nb complex and extends above $E_F$. Cr 3$d$ states (highlighted by orange) show large exchange splitting: most of the spin-down states are pushed above $E_F$. Both spin channels (up and down) are metallic.

The Figure 4 also demonstrates that for $P6_322$–II crystal structure, where the unit cell contains two nonequivalent positions of Cr atoms, the density of states corresponding to the Cr 3$d$ orbitals is distributed showing no clear distinct peaks as it for both $P6_322$–I and $P6_3/mmc$. This result indicates that the different arrangement of Cr atoms intercalated into the lattice can alter the features of their distribution of state.

For all systems under consideration each Cr atoms has six nearest Se and two Nb atoms. In CrSe$_6$–Nb$_2$ cluster unit the local symmetry around Cr is
approximately $D_{3d}$ and the Cr 3$d$ states are split into $t_{2g}$ (which is further split into $a_{1g}$ and $e'_g$) and $e_g$ states.

Each Nb atom is in trigonal prismatic coordination with six Se neighbors. So, the Nb 4$d$ states are split into $a_{1g}$ ($d_{z^2}$) state, $e'_g$ doublet ($d_{xy}$, $d_{x^2−y^2}$), and $e_g$ doublet ($d_{yz}$, $d_{zx}$).

The Figures 5, 6 show partial $d$-wave densities of state projected onto Nb and Cr harmonics for spin up and spin down, respectively.

We start our discussion from the spin-down channel, where the occupied states from $−2$ eV and above are predominantly Nb $a_{1g}$ and $e'_g$ orbitals. The exchange splitting pushes most of the spin-down Cr 3$d$-states above $E_F$.

In the spin-up channel, for all structures under consideration, the chromium $e'_g$-states form a sharp peak below $E_F$ in a narrow energy region from $−2$ to $−1$ eV. The Cr $a_{1g}$ and $e_g$-states have weak distributed character in a wide energy range, extending across $E_F$. The delocalization of $a_{1g}$-state is a consequence of strong hybridization with Nb 4$d$-orbitals.

**Fig. 5** Partial $d$-wave density of states projected onto Nb and Cr harmonics (spin-up). Energy 0 refers to the Fermi level. Note that the vertical scale is different in each panel.
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The strong hybridization of chromium $a_{1g}$-state with Nb $4d$-orbitals for Cr$_x$NbSe$_2$ compounds (with $x = 0.33$ and $x = 0.5$) was also obtained in [7], where the NMR spectra measurements were performed on the $^{53}$Cr and $^{93}$Nb nuclei. The $^{93}$Nb NMR spectra in both Cr$_{0.33}$NbSe$_2$ and Cr$_{0.5}$NbSe$_2$ in zero external magnetic field have peaks, which are equal to the local field about 160.0 kOe and 158.1 kOe, correspondingly. This local field on niobium nuclei is induced by the Cr ions and could be the result of hybridization of $3d_{z^2}$ orbitals with niobium $4d$ orbitals.

The $^{53}$Cr NMR spectrum in Cr$_{0.33}$NbSe$_2$ and Cr$_{0.5}$NbSe$_2$ are different. The sample with $x = 0.5$ was fitted by one line while the sample with $x = 0.33$ was described by the superposition of two quadrupole split lines. Ogloblichev et al [7] proposed that the existence of these two lines in Cr$_{0.33}$NbSe$_2$ indicates the presence of two chromium ions positions with different nearest magnetic or charge environment in the structure.
3.3 Quadrupole hyperfine interactions

The nuclear magnetic resonance spectrum is determined by the hyperfine interaction. The hyperfine interaction Hamiltonian in 3d-transition metals is defined as [15]

$$\hat{H} = \hat{H}_{\text{mag}} + \hat{H}_{\text{el}},$$

(1)

Here $\hat{H}_{\text{el}}$ is the electric hyperfine interaction, $\hat{H}_{\text{mag}}$ is the magnetic hyperfine interaction. The correct comparison between the calculated and experimental data is given by parameters that determine the hyperfine structure of the spectrum: magnetic hyperfine coupling and nuclear quadrupole interaction constants. These constants occur in the formula terms of the spin Hamiltonian (1), within the framework of which the spectrum is interpreted.

The electron hyperfine interaction $\hat{H}_{\text{el}}$ is characterized by the frequency of the quadrupole resonance, $\nu_Q$. In the coordinate system associated with the principal axes of the electric field gradient tensor, the value of $\nu_Q$ is determined by the expression

$$\nu_Q = \frac{3eQ|V_{ZZ}|}{2I(2I - 1)h}.$$  

(2)

Here $h$ is Planck’s constant, $e$ is electron charge, $I$ is the nuclear spin ($I = 9/2$ for $^{93}\text{Nb}$, $I = 3/2$ for $^{53}\text{Cr}$). $Q$ is the nuclear quadrupole moment, $V_{ZZ}$ represents the components of the electric field gradient tensor, $V_{\text{eff}}$, in the principal axes ($|V_{XX}| < |V_{YY}| < |V_{ZZ}|$).

The parameters of quadrupole interactions of chromium and niobium were determined by the first-principles calculations for the crystal structures $P6_3/mmc$, $P6_322$-I, and $P6_322$-II with different environments of chromium atoms in the lattice (see Table 1).

First of all we begin from discussion of results for $^{53}\text{Cr}$ nuclei. It was determined that for all structures under consideration the principal axis of the electric field gradient $V_{ZZ}$ is directed along the $c$ axis and has the symmetry parameter $\eta$ close to zero.

<table>
<thead>
<tr>
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<th>$P6_322$-I</th>
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<th>$P6_322$-II</th>
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<td>$^{53}\text{Cr}$</td>
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<td>$^{53}\text{Cr}$</td>
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<td>$^{53}\text{Cr}$</td>
<td>$^{93}\text{Nb}$</td>
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<td>1.19</td>
<td>0.89</td>
<td>2.53</td>
<td>2.19</td>
<td>0.61</td>
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An analysis of the data in Table 1 shows that the ab initio calculations give a values for $^{53}\nu_Q$ that are different for various chromium environment in crystal lattice. So, for the space group $P6_3/mmc$, where ordering of Cr atoms leads to
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the formation of 2×2 superstructure, the value of nuclear quadrupole frequency is about 1.04 MHz that is two times less than for the space group P6\textsubscript{3}22. Comparison of $\nu_Q$ for P6\textsubscript{3}22-I and P6\textsubscript{3}22-II crystal structures shows that the values are close to each other. Moreover, for crystal structure, where the coexistence of regions with orderings of the 2×2 and $\sqrt{3} \times \sqrt{3}$ type of Cr atoms takes place, there are two nonequivalent chromium positions in the structure with slightly different values of $^{53}\nu_Q$. The nuclear quadrupole frequency value for chromium position 2d, which corresponds to the formation of the $\sqrt{3} \times \sqrt{3}$ superstructure, is smaller than for chromium position 2c corresponding to the formation of the 2 × 2 superstructure. Our results are in agreement with that obtained from the NMR experiment. So, as noticed above in 3.2, the Cr\textsubscript{0.5}NbSe\textsubscript{2} sample was fitted by one line and observed value of quadrupole frequency $^{53}\nu_Q^{exp}$ is equal 3.82 MHz that correlates with $^{53}\nu_Q^{calc} = 2.85$ MHz obtained for P6\textsubscript{3}22-I crystal structure. The Cr\textsubscript{0.33}NbSe\textsubscript{2} sample was fitted by two lines with $^{53}\nu_Q^{exp}(1) = 1.24$ MHz and $^{53}\nu_Q^{exp}(2) = 3.82$ MHz that correlate with our DFT results for structures with ordering of Cr atoms forming the 2×2 superstructure and $\sqrt{3} \times \sqrt{3}$ superstructure, correspondingly. Thus, our first-principles calculations confirmed the assumption of Ogloblichev et al [7] for Cr\textsubscript{0.33}NbSe\textsubscript{2} about the coexistence of regions with superstructures described by space groups P6\textsubscript{3}/mmc and P6\textsubscript{3}22.

Next, we will discuss the results of our first-principles calculations for $^{93}$Nb nuclei. For all structures under consideration we obtained that i) the main axis of the electric-field gradient $V_{ZZ}$ on niobium nuclei is directed along the c axis with asymmetry parameter $\eta$ close to zero; ii) there are two different values for the quadrupole frequency corresponding to nonequivalent positions of Nb atoms in the crystal lattice; iii) the distribution of $^{93}\nu_Q^{calc}$ values from ~0.6 MHz to ~1.2 MHz. Our calculated results differ from experimental one more than four times. It can be attributed to the inhomogeneous distribution of chromium ions over the lattice. Such distribution significantly complicates the indication of the crystal lattice for calculations.

At the discussion of the local field on niobium nucleus in Cr\textsubscript{x}NbSe\textsubscript{2} Ogloblichev et al [7] proposed that for the creation of the field the presence of a magnetic moment about $\approx 0.46\mu_B$ in the Nb 4d shell is required. According to our calculation data for magnetic moments on niobium nuclei it values is distributed from $\sim 0.03\mu_B$ to $\sim 0.29\mu_B$ depending on the chromium environment in the crystal lattice. So, we can indirectly confirm the conclusion of author’s [7] about the creation of the local field on niobium nuclei by chromium ions.

We also calculated the values of magnetic moments on chromium atoms. For all structures, $\mu_{calc}$ is about $3\mu_B$ which is in agreement with data obtained earlier [11]–[13].

4 Conclusion

The first-principles calculations were performed to determine the electronic structure and obtain the parameters of the quadrupole interaction of chromium.
Electronic Structure and Hyperfine Interactions in \(\text{Cr}_x\text{NbSe}_2 (x = 0.33, 0.5)\) by DFT and niobium nuclei in compounds \(\text{Cr}_x\text{NbSe}_2 (x = 0.33, 0.5)\) for the crystal structures \(P6_3/mmc\) (when the ordering of Cr atoms leads to the formation of \(\sqrt{3} \times \sqrt{3}\) superstructure;) and \(P6_3\text{22}\) (with two possible orderings of chromium atoms: \(P6_3\text{22-I}\), where the ordering of Cr atoms leads to the formation of \(2 \times 2\) superstructure; \(P6_3\text{22-II}\), where the coexistence of regions with orderings of the \(2 \times 2\) and \(\sqrt{3} \times \sqrt{3}\) type of Cr atoms takes place. The results are discussed together with the data obtained by the nuclear magnetic resonance method on \(^{53}\text{Cr}\) and \(^{93}\text{Nb}\) nuclei in [7]. As a result of the work, the following main results can be distinguished:

1. The structure of \(\text{Cr}_{0.33}\text{NbSe}_2\) is described with two chromium sites with a crystalline environment corresponding to the \(P6_3/mmc\) and \(P6_3\text{22}\) structures. The \(\text{Cr}_{0.5}\text{NbSe}_2\) structure can be described with equivalent chromium positions with an environment corresponding to the \(P6_3\text{22}\) structure.

2. High hybridization of chromium and niobium orbitals with a hyperfine magnetic moment on niobium from 0.03\(\mu_B\) to \(\sim 0.29\mu_B\) was obtained in all calculated crystal structures, which is qualitatively confirmed by the large value of the local field on the niobium nucleus according to NMR data.

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Declarations

- **Declaration of Competing Interest.** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
- **Availability of data and materials.** Data will be made available on request.
- **Authors’ contributions.** Polina Agzamova: Conceptualization, Investigation, Writing. Vasily Ogloblichev: Conceptualization, Supervision.

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