Defect-Induced Magnetism in Two-Dimensional NbSe₂

P. Manchanda^{1,2} and R. Skomski²

¹ *Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235.*

² *Department of Physics and Astronomy and Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, NE 68588, United States.*

Abstract

The energetics and magnetism of perfect and vacancy-containing two-dimensional NbSe₂ monolayers is investigated by first-principle calculations. It has been found the single Se vacancy has the lowest formation energy. Perfect NbSe₂ monolayers, as well as monolayers containing single-selenium and double-selenium vacancies, are nonmagnetic metallic. However, Nb vacancies create a magnetic moment of $1.5 \mu_B$ per vacancy. The moment is highly localized, confined nearly exclusively on the Se atoms adjacent to the vacancy, and mainly originates from the Se 4p electrons. The moment distribution indicates strongly anisotropic exchange bonds between vacancy moments.

1. Introduction

The interplay between magnetism and superconductivity in NbSe₂ has recently attracted much attention [1, 2, 3]. The research forms part of the "beyond graphene" research effort and is rooted in the versatile electronic properties of transition-metal dichalcogenide (TMD) monolayers, which range from metallic [4, 5] and semiconducting [6] to superconducting [7]. Some of these two-dimensional TMDs exhibit outstanding physical properties, such as high room-temperature electron mobility and electronic band gaps in the visible range, and are therefore of interest for applications in transistors [8, 9], catalysis [10], magnetooptical [11] and optoelectronic [12, 13] devices, and energy storage [14, 15]. Furthermore, TMD monolayers can be synthesized fairly easily using mechanical or solvent-based exfoliation methods [16, 17].

An important aspect of the behavior of NbSe₂ monolayers is their magnetism. Pristine NbSe₂ monolayers, Fig. 1(a), are nonmagnetic, as are most other TMD monolayers, including the well-investigated dichalcogenide MoS₂. However, magnetism can be created in two-dimensional TMDs by methods such as edge structuring [18, 19], defect introduction [20, 21], doping with transition metal impurities [22, 23], application of external electric fields [24], strain engineering [25, 26], and chemical functionalization [27-29]. In NbSe₂, ferromagnetism has recently been achieved chemically, using hydrazine molecules [1].

In this paper, we use density-functional calculations to investigate another source of magnetism in NbSe₂, namely vacancy defects. Vacancies are common in TMD thin films, caused by imperfect film growth [30, 31, 32] and significantly influencing the electronic and magnetic properties of monolayers [20, 33-36]. For example, ferromagnetism is created by sulfur vacancies in semiconducting MoS₂ [37]. Such vacancy effects are particularly important in NbSe₂, due to the involvement of both magnetic and superconducting states.

Fig. 1. Pristine NbSe₂ monolayers: (a) top and side view of atomic structure and (b) electronic structure.

2. Computational details

Our first-principle calculations were performed using the projector-augmented wave (PAW) method [38] with a plane-wave basis set, as implemented in the Vienna *ab-initio* simulation package (VASP) [39, 40]. We use the generalized gradient approximation (GGA) and employ Perdew-Burke-Ernzerhof (PBE) exchange and correlation functionals [40]. The kinetic energy cutoff of 520 eV were used for all the calculations, and the convergence criterion of the self-consistent field calculations were set to 10^{-5} eV. For all calculations, we have used a 5×5 supercell, as in Fig. 1(a), and a vacuum spacing of about 15 Å to avoid the interaction between neighboring periodic images. The atomic positions were allowed to relax using conjugate-gradient techniques until the force on each atom is less than 0.01 eV/Å.

3. Results and Discussion

Before considering the defects in NbSe₂ monolayers, we first discuss the properties of pure NbSe₂ monolayers. The calculated lattice constant is 3.48 Å, which are in good agreement with experimental value for NbSe₂ bulk [42]. The most stable configuration of NbSe₂ monolayer is non-magnetic and metallic. Figure 1(b) shows the calculated band structure, in which the band state crossing the Fermi level is mainly originated from *d* states of Nb atom.

We have studied various possible vacancies V in NbSe_2 monolayers, including Nb (V_{Nb}), monoselenium (V_{Se}), diselenium (V_{Se_2}) and two-monoselenium ($V_{\text{Se}+\text{Se}}$) vacancies, as well as a vacancy complex consisting of one Nb and neighboring diselenium vacancy (V_{NbSe_2}) and a vacancy complex of Nb and nearby three monoselenium vacancy (V_{NbSe_3}). Figure 2 shows all these vacancies.

Fig. 2. Atomic structures of the vacancies considered in this paper: (a) Nb vacancy V_{Nb} , (b) monoselenium vacancy V_{Se} , (c) diselenium vacancy V_{Se_2} , (d) two-monoselenium vacancy $V_{\text{Se}+\text{Se}}$, (e) vacancy complex V_{NbSe_2} , and (f) V_{NbSe_3} .

The relative stability of these defects can be determined by calculating formation energy using following equation:

$$E_f = E_{\text{total}}(\text{defect}) - [E_{\text{total}}(\text{pristine}) + \sum_i n_i \mu_i] \quad (1)$$

where $E_{\text{total}}(\text{defect})$ and $E_{\text{total}}(\text{pristine})$ is the total energy of the supercell with and without defects. n_i denotes the number of atoms added or removed (with the negative sign) from the pristine surfaces to create defects and μ_i is the chemical potential

In a thermal equilibrium the chemical potential of NbSe₂ monolayers should satisfy, $\mu_{\text{NbSe}_2} = \mu_{\text{Nb}} + 2\mu_{\text{Se}}$, where μ_{Nb} and μ_{Se} are the chemical potentials for Nb and Se, respectively. The defect formation energies as a function of Se chemical potential, over wide range of experimental conditions from Nb-rich to Se-rich conditions are shown in Fig. 3. For Nb-rich environment, $\mu_{\text{Nb}} = E_{\text{tot}}(\text{Nb})$, where $E_{\text{tot}}(\text{Nb})$ is the total energy of Nb per atom in bulk form. Therefore, $\mu_{\text{Se}} = (\mu_{\text{NbSe}_2} - \mu_{\text{Nb}})/2$. For Se-rich environment, $\mu_{\text{Se}} = E_{\text{tot}}(\text{Se})$, where $E_{\text{tot}}(\text{Se})$ is the total energy of bulk Se. Thus, μ_{Se} is calculated as $\mu_{\text{Nb}} = \mu_{\text{NbSe}_2} - 2\mu_{\text{Se}}$.

Fig. 3. Formation energies of various defects as a function of the Se chemical potential.

It can be seen that the formation energy of V_{Se} is lowest for both Nb-rich and Se-rich condition. Therefore, Se vacancies are very likely to form during mechanical exfoliation experiment. The comparison of the formation energies of $V_{\text{Se+Se}}$ and V_{Se_2} defect shows that the formation of $V_{\text{Se+Se}}$ defect is more favorable as compared to V_{Se_2} . Re vacancy has large formation energy as compared to V_{Se} even in Se-rich condition. At Nb-rich condition the defect formation energy of V_{NbSe_3} is lower than the formation energy of V_{Nb} , this means that once the Nb vacancy is formed the surrounding Se can be easily removed. However, the defect formation energy of V_{NbSe_2} is largest for the whole chemical potential. The defects can alter the electronic and magnetic properties significantly.

Our calculations show that neither Se nor Se_2 and Se+Se vacancies yield a magnetic moment and remains metallic. However, Nb vacancies create a magnetic moment of $1.5 \mu_B$ per missing Nb atom, supported by an energy difference of 86 meV between the magnetic and non-magnetic states. Figure 4 shows the spatial origin of the vacancy moment: the moment distribution (magnetization) is nearly exclusively created by the $4p$ orbitals of the selenium atoms adjacent to vacancy. This picture is confirmed by the orbital projected local density of states (DOS). Figure 5 shows the corresponding DOS for the Se atoms marked by the gray background in Fig. 4. The atom's $4p_x$, $4p_y$, and $4p_z$ orbitals hybridize in a way that causes the magnetization distribution to point towards the vacancy.

Fig. 4. Magnetization density (red) around a Nb vacancy.

From the densities of states we also see that the magnetic moment arises is associated with the splitting of a very narrow $4p$ peak near the Fermi level. The moment formation is facilitated by the height of the peak, which makes it easy to satisfy the Stoner criterion. The narrow character of the peak also indicates that the impurity moment is fairly localized, although the one-electron character of the wave functions used to evaluate the density functional does allow the establish true localization.

Fig. 5. Orbital projected local densities of states for the marked Se atom in Fig. 4.

The character of the moment, realized by p electrons rather than d electrons, is reminiscent of the behavior oxides and some other materials [43, 44], where defects create moments in otherwise nonmagnetic materials. The exchange interaction between different Nb vacancies and their interference with possible charge-density waves, as they exist in bulk NbSe₂ [45], as well as their effect on superconductivity, are a challenge for future research. However, Fig. 4 reveals that the small magnetic moments on the Nb atoms farther distant from the vacancy do not surround the vacancy isotropically but exhibit a pronounced threefold symmetry that mirrors the directional moment distribution on the Se atoms. This feature is likely to give rise to anisotropic exchange bonds, because exchange interactions are realized through the overlap of spin-polarized orbitals [46].

4. Conclusions

In summary, we have investigated how the energetics, electronic structure and magnetism of NbSe₂ monolayers are affected by vacancies. We found that single Se vacancy is likely to form whereas the formation energy of Nb vacancy is large. Perfect monolayered NbSe₂ is nonmagnetic metallic, and the same is true for Se vacancies. By contrast, Nb vacancies create a magnetic moment of $1.5 \mu_B$ per missing Nb atom. The magnetic moment resides nearly exclusively on the atoms adjacent to the vacancy and is caused by Se $4p$ electrons. The residual moment on more

distant atoms exhibits a pronounced three-fold symmetry, which likely implies anisotropic exchange bonds.

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