Atomic-scale defects in the two-dimensional ferromagnet CrI$_3$ from first principles

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Abstract

The family of atomically thin magnets holds great promise for a number of prospective applications in magneto-optoelectronics, with CrI$_3$ arguably being its most prototypical member. However, the formation of defects in this system remains unexplored to date. Here, we investigate native point defects in monolayer CrI$_3$ by means of first-principles calculations. We consider a large set of intrinsic impurities and address the atomic structure, thermodynamic stability, diffusion and aggregation tendencies as well as local magnetic moments. Under thermodynamic equilibrium, the most stable defects are found to be either Cr or I atomic vacancies along with their complexes, depending on the chemical potential conditions. These defects are predicted to be quite mobile at room and growth temperatures, and to exhibit a strong tendency to agglomerate. In addition, our calculations indicate that the deviation from the nominal stoichiometry largely impacts the magnetic moments, and the defect-induced lattice distortions can drive local ferromagnetic-to-antiferromagnetic phase transitions. Overall, this work portrays a comprehensive picture of intrinsic point defects in monolayer CrI$_3$ from a theoretical perspective.

Keywords: 2D materials, disorder, quantum magnetism

1. Introduction

Atomically thin magnets have recently joined the ever-growing family of two-dimensional materials, and are currently emerging as suitable candidates for novel magneto-optoelectronics devices in the ultimate limit of atomic thickness [1–5]. Among them, ultrathin films of CrI$_3$ have attracted a great deal of interest due to the extensive control that can be achieved over their magnetic properties [5–9]. In particular, such films have been isolated upon exfoliation from their layered bulk counterpart, and consist of a honeycomb network of Cr$^{3+}$ ions sandwiched between a pair of atomic planes of I ligands [5, 10]. The intrinsic magnetism of bulk CrI$_3$ is preserved when the crystal is thinned to the few-layer and eventually single-layer regime of thickness, owing to the key role played by the single-ion anisotropy which prevents thermal fluctuations to quench the magnetically ordered phases up to 45 K [5, 11]. While in ultrathin films of CrI$_3$ both in-plane ferromagnetic and off-plane antiferromagnetic interactions coexist [5, 12], in the single-layer regime the exchange interactions are restricted to the in-plane direction solely, where Cr$^{3+}$ ions act as spin-3/2 centers and couple ferromagnetically through I-mediated super-exchange channels [13, 14].

Under thermodynamic equilibrium conditions, the entropic contribution to the overall free energy of a solid is responsible for the ubiquitous presence of defects at finite temperatures. Although disorder often affects the properties of materials in a detrimental manner, in many cases the incorporation of a certain amount of impurities has proven instrumental in expanding the functionalities of the hosting system. This is especially true in ultrathin crystals, where the reduced dimensionality of
the lattice enhances the impact of imperfections [15, 16], as it has been demonstrated, e.g. for elemental monolayers like graphene [17–21], silicene [22–24] or phosphorene [25, 26], as well as transition metal dichalcogenides [27–32]. However, the role of defects in atomically thin magnets remains entirely unexplored to date.

In this paper, we investigate the formation of intrinsic defects in monolayer CrI₃ by means of first-principles calculations. We address the atomic structure, thermodynamic stability, diffusion and aggregation tendencies along with the defect-induced magnetic moments of a large set of native impurities, including vacancy, adatom, self-interstitial and antisite defects. Overall, this work offers a theoretical insight into defects formation in monolayer CrI₃ and further lays the foundation for defect engineering in this prototypical two-dimensional magnet.

2. Methodology

Our first-principles calculations are performed within the spin-polarized density functional theory formalism, as implemented in the Vienna Ab Initio Simulation Package (VASP) [33, 34]. The exchange and correlation effects are treated under the generalized gradient approximation devised by Perdew, Burke, and Ernzerhof (PBE) [35]. In the case of pristine and defective supercells of CrI₃, this functional is supplemented with an on-site Coulomb repulsion term \( U = 1.5 \text{ eV} \) acting on the \( d \) shell of Cr atoms [36]. The resulting PBE+\( U \) density functional was shown to provide an excellent description of the magnetic properties of monolayer CrI₃, as demonstrated by the comparison with higher-level many-body wavefunction results and available experimental data [5, 14, 37].

Electron-core interactions are described through the projector-augmented wave method, while the Kohn-Sham wavefunctions for the valence electrons are expanded in a plane wave basis with a cutoff on the kinetic energy of 400 eV. The integration over the first Brillouin zone is carried out using the equivalent of \( 12 \times 12 \) \( k \)-points per unit cell. The atomic coordinates are optimized until the maximum component of the Hellmann–Feynman forces are smaller than 0.02 eV Å \(^{-1} \), while constraining the lattice constant to the experimental value of 6.867 Å. The saddle points for the determination of the energy barriers are located with the help of the climbing-image nudged elastic band method [38]. Specifically, we have optimized under the appropriate constraints the intermediate image between the initial and the final states until forces converged to 0.04 eV Å \(^{-1} \). Similarly to our previous work [39], magnetic exchange interactions have been calculated following the well-established four-state method for energy-mapping analysis [40, 41].

We model defective lattices by introducing point defects in otherwise pristine \( 4 \times 4 \) hexagonal supercells of monolayer CrI₃ containing 128 atoms. A vacuum region 17 Å thick is included to avoid artificial interactions between periodic replicas.

3. Results and discussion

We start by examining the stability of native defects in monolayer CrI₃. We consider a broad set of different point defects, the atomic structure of which is shown in figure 1. The investigated defects belong to three classes, namely (i) vacancy defects, including atomic vacancies (V₄ or V₃) along with their complexes V₄I₃ and V₃I₄, (ii) adatom defects, consisting of excess atoms located on top of either chromium (Cr⁺) or iodine lattice site (I⁺ and I⁻), and (iii) antisite (Cr⁻ and I⁺) or self-interstitial (Cr⁺ and I⁻) defects, depending on whether the extra Cr and I atoms are located in an occupied or unoccupied site, respectively.

Under thermodynamic equilibrium, the quantity of primary interest in governing the relative stability of defects is their formation energy \( E_{\text{form}} \). Given that CrI₃ is a binary system, in most cases the introduction of intrinsic defects is accompanied by a deviation from the nominal stoichiometry, thereby rendering \( E_{\text{form}} \) dependent on chemical potentials of the constituent elements. For charge-neutral defects at zero Kelvin and standard pressure, the formation energy takes the form

\[
E_{\text{form}}(\mu) = E_{\text{defect}} - E_{\text{host}} - \sum_i n_i \mu_i
\]

(1)

with \( E_{\text{defect}} \) and \( E_{\text{host}} \) being the total energies of the defective and pristine supercell, respectively, \( n_i \) the number of atoms that one has to add to or remove from the lattice in order to create the defect, and \( \mu_i \) the corresponding chemical potential. As is customary, we assume that Cr and I are in thermal equilibrium with monolayer CrI₃ through to the expression

\[
\mu_{\text{CrI}_3} = \mu_{\text{Cr}} + 3 \mu_{\text{I}}.
\]

(2)

\[\text{Figure 1. Atomic structure of the point defects in monolayer CrI}_3\text{ considered in this work. Blue and orange balls represent Cr and I atoms, respectively.}\]
The relevant interval of chemical potential in which defect formation energies are physically meaningful spans the energy range in which monolayer CrI$_3$ remains stable against the decomposition into its elemental constituents. These are taken to be the lowest-energy phases of these chemical elements, namely the bcc Cr crystal and the isolated I$_2$ molecule. Within this formalism, the range of stability of monolayer CrI$_3$ is $-0.77 \text{ eV} < \mu_I < 0 \text{ eV}$.

In figure 2, we overview the formation energy of the point defects shown in figure 1 as a function of the I chemical potential. Although the relative stability of the defects is largely ruled by the chemical potential, our calculations reveal that either atomic vacancies or their complexes exhibit the lowest formation energies. Specifically, I-rich conditions promote the formation of V$_{\text{CrI}}$ and V$_{\text{CrI6}}$ defects, whereas I-poor conditions enhance the stability of V$_I$ and V$_{\text{CrI6}}$ ones. This result demonstrates that, when thermodynamic equilibrium prevails, monolayer CrI$_3$ is likely to exhibit a sub-stoichiometric composition.

As far as the metastable defects are concerned, we found that I adatoms display lower formation energies than Cr adatoms over the entire range of chemical potential. However, while the binding of an extra I atom on top of an I site is more stable than on top of a Cr site by 0.55 eV, the opposite behavior is observed for an extra Cr atom, being Cr$_{\text{b}}$I$_1$ lower in energy than Cr$_1$ by 1.15 eV. Differently from adatom defects, the relative stability of self-interstitials is dominated by the chemical potential conditions. In fact, the I$_i$ defect remains the most stable self-interstitial defect only under I-rich conditions, as approaching I-poor conditions stabilizes the formation of the Cr$_i$ defect. It is worth noticing that, while excess I atoms incorporate into monolayer CrI$_3$ as adatom defects (i.e. I$_1$ is more stable than I$_i$ by 0.82 eV), excess Cr atoms should instead be accommodated in the lattice as self-interstitials (i.e. Cr$_i$ is more stable than Cr$_{\text{b}}$I$_1$ by 1.06 eV). The relative stability of antisites is also governed by chemical potential conditions, as I-rich (I-poor) conditions stabilize the IC$_i$ (Cr$_i$) defect. We notice that the formation energy of both the antisite defects considered is larger than the sum of the formation energy of an isolated vacancy and an isolated adatom by 0.40 eV and 0.05 eV for IC$_i$ and Cr$_i$ defects, respectively. This indicates that vacant sites enhance the reactivity of the lattice as compared to the pristine areas of the monolayer.

We now turn our attention to the mobility of atomic vacancies. As we discussed above, these defects exhibit the lowest formation energy in a quite broad range of chemical potential and further constitutes the building blocks for the also stable vacancy complexes V$_{\text{CrI3}}$ and V$_{\text{CrI6}}$. In figure 3(a), we give the energy barriers for a V$_I$ to diffuse to the three nearest neighboring I sites. Specifically, we consider diffusion processes to either the I atom bridging the same (path 1) or the nearest (paths 2 and 3) pair of Cr atoms between which V$_I$ is introduced. We found that V$_I$ features a diffusion barrier in the 0.73–1.03 eV range, depending on the path considered, with path 2 being the most energetically favorable. Furthermore, we determine the energy barrier for a V$_{\text{Cr}}$ defect to diffuse to the nearest equivalent to be 1.05 eV, as we show in figure 3(b). We estimate the diffusion coefficient $D$ of vacancy defects as

$$D = d^2 \nu \exp \left[ \frac{-E_{\text{barr}}}{k_B T} \right]$$  \hspace{1cm} (3)$$

with $E_{\text{barr}}$ being the energy barrier for vacancy defects to diffuse (see figure 3), $T$ the considered temperature, $k_B$ the Boltzmann constant, $d$ the hopping distance and $\nu$ the vibrational frequency, typically in the order of $10^{12}$ s$^{-1}$. Notice that, in the above expression, a negligible change in entropy between the initial and the transition states is assumed. At $T = 300 \text{ K}$, we find $D \approx 10^{-15}$ cm$^2$ s$^{-1}$ for V$_I$ (along the favorable path 2) and $D \approx 10^{-21}$ cm$^2$ s$^{-1}$ for V$_{\text{Cr}}$. These diffusion coefficients increase to $D \approx 10^{-11}$ cm$^2$ s$^{-1}$ and $D \approx 10^{-15}$ cm$^2$ s$^{-1}$, respectively, at $T = 450 \text{ K}$, i.e. the temperature at
which molecular-beam epitaxy experiments are carried out [42], hence indicating a certain degree of mobility of these defects under epitaxial growth conditions.

Next, we investigate the tendency of vacancy defects to coalesce. To this end, we quantify the agglomeration energy \( E_b \) of a given defect complex \( AB \), formed upon clustering of the otherwise spatially separated \( A \) and \( B \) defects, by comparing their formation energies as

\[
E_b = E_{\text{form}}(A) + E_{\text{form}}(B) - E_{\text{form}}(AB). \tag{4}
\]

According to this expression, positive (negative) values of \( E_b \) point towards an energetically favorable (unfavorable) tendency of defects to aggregate. In figures 4(a),(b), we show the agglomeration energies to form a secondary vacancy defect at several lattice sites neighboring the first missing atom. For the \( I \) divacancies case shown in figure 4(a), we find that, depending on the site considered, the introduction of a secondary \( V_1 \) can be either energetically favorable (sites 1 and 4) or unfavorable (sites 2 and 3), with the agglomeration energy attaining its maximum upon formation of a secondary \( I \) vacancy at site 1. This is in contrast with the formation of a second

\[
\begin{array}{c|c|c}
\text{Point defect} & \Delta \mu (\mu_B) & \text{Point defect} \\ 
V_1 & 1.00 & Cr^{Cr} \\ 
V_{Cr} & -6.00 & Cr^I \\ 
V_{Cr3} & -3.00 & Cr^I \\ 
V_{Cr6} & 0.00 & I_x \\ 
V_{2I} & 2.00 & I_{Cr} \\ 
V_{2Cr} & -12.00 & Cr^I \\ 
I^f & 1.00 & I^f \\ 
\end{array}
\]

Table 1. Difference in local magnetic moments between pristine and defective monolayers of CrI (\( \Delta \mu \)).

Finally, we discuss the effect of point defects on the magnetism of CrI. Table 1 lists the difference in magnetic moments between pristine (i.e. 3 \( \mu_B \) per Cr\(^{3+} \) ion, in accord with experiments [5]) and defective lattice, this latter hosting the defects studies in this work. Remarkably, we notice that all defects but \( V_{Cr6} \) affect the magnetism of monolayer CrI, thereby suggesting that deviations from the nominal stoichiometry are likely to be accompanied by an alteration of the local magnetic moments. Specifically, \( V_1 \) and \( V_{Cr} \) defects lead to a \( \Delta \mu \) of \(-1.00 \mu_B \) and \( 6.00 \mu_B \), respectively. These values double when considering \( V_{2I} \) and \( V_{2Cr} \) defects, irrespectively of the relative positions of the missing pair of atoms. The \( \Delta \mu \) associated with the \( V_{Cr3} \) complex is \(-3.00 \mu_B \). Excess Cr or I atoms, whether as adatom or self-interstitial defects, change the intrinsic magnetic moments by \( 6.00 \mu_B \) and \( 1.00 \mu_B \), respectively, while antisite \( I_{Cr} \) (Cr\(^I \)) defect induces a larger \( \Delta \mu \) of \(-5.00 \mu_B \) (7.00 \( \mu_B \)).

Point defects lead to local distortions of the atomic structure of monolayer CrI, possibly affecting the magnetic exchange interactions in their vicinity. In a recent work [39], it has been shown that lattice deformations can modulate the magnetic ground state of monolayer CrI to a large extent, with a ferro-to-antiferromagnetic crossover taking place upon the reduction of the Cr-I-Cr bond angle below \( \approx 88^\circ \). Among the thermodynamically stable defects which form in monolayer CrI (see figure 2), \( V_{Cr6} \) is the one inducing the most substantial
lattice distortion. Indeed, it gives rise to two structurally inequivalent Cr-Cr bonds, which correspond to the $d_1$ (with $d_{Cr-Cr} = 3.69$ Å and $\angle Cr-I-Cr = 85^\circ$) and $d_2$ (with $d_{Cr-Cr} = 3.92$ Å and $\angle Cr-I-Cr = 92^\circ$) bonds schematically depicted in figure 5. These structural parameters have to be compared with those of pristine CrI$_3$, i.e. $d_{Cr-Cr} = 3.96$ Å and $\angle Cr-I-Cr = 93^\circ$, for which a Heisenberg exchange coupling $J = -1.44$ meV has been reported [14]. We assess the role of V$_{CrI6}$ defect and the ensuing local distortion of the atomic structure on the magnetism of monolayer CrI$_3$ by determining the Heisenberg exchange couplings along the two inequivalent Cr-Cr bonds. While the exchange coupling associated with the $d_2$ bond ($J = -1.34$ meV) is found to be almost unchanged w.r.t. the pristine monolayer, a weak antiferromagnetic coupling ($J = 0.08$ meV) emerges along the $d_1$ bond, hence revealing a local magnetic-phase transition driven by the defect-induced lattice distortions. Overall, this finding paves the way towards defect-engineering of monolayer CrI$_3$, in which antiferromagnetic domains embedded in a ferromagnetic matrix may be realized through structural deformations caused by impurities. [43].

4. Conclusion

In summary, we have carried out extensive first-principles calculations to investigate the formation of native defects in the prototypical two-dimensional magnet CrI$_3$. Depending on the chemical potential conditions, we have identified mobile V$_I$ and V$_Cr$ species along with their complexes V$_{CrI3}$ and V$_{CrI6}$ as the most stable defects, these latter emerging as a consequence of the strong agglomeration tendency. Our results indicate that, under thermodynamic equilibrium, monolayer CrI$_3$ should exhibit a sub-stoichiometric nature, which in turn is found to locally affect the magnetic moments and Heisenberg exchange couplings. To conclude, our findings pinpoint a marked interplay between atomic-scale disorder and magnetism in monolayer CrI$_3$.

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Figure 5. Atomic and magnetic structure of the V$_{CrI6}$ defect in monolayer CrI$_3$. Blue and red balls represent Cr sites carrying opposite magnetic moments. Also given are the $d_1$ and $d_2$ bonds in the vicinity of the defect, along which antiferromagnetic and ferromagnetic couplings are predicted, respectively.
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