Study of the exfoliation of two-dimensional Cu-doped $TiSe_2$

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Materials with thicknesses ranging from a few nanometers to a single atomic layer present unprecedented opportunities to investigate matter properties restricted to the two-dimensional plane. One of the most studied two-dimensional materials are the so-called transition metal chalcogenides (TMD). Among these materials, titanium diselenide (TiSe2) and its derivatives stand out due to their well-known physical properties. However, certain aspects of their behavior still pose challenges to current theoretical knowledge, leading to difficulties or delays in their application. Jurelo et al. [1] studied through density functional theory (DFT) calculations the effect of copper (Cu) intercalation on the structural, vibrational and electronic properties of TiSe2, observing that it exhibits properties akin to those of a high-temperature superconductor. In general, the synthesis of two-dimensional $TiSe_2$ is performed by chemical vapor deposition (CVD), mechanical exfoliation, or liquid phase exfoliation. To overcome the complexity and cost of these processes Rosa et al. [2] developed a novel method that consists of synthesizing and isolating single 2D sheets from 3D Cu_xTiSe_2 crystals, through a solvothermal exfoliation process using hydrazine (N_2H_4) as a solvent. It was observed that N_2H_4 facilitates exfoliation while preserving the structure of Cu_xTiSe_2 [2].

With the goal of understanding how N_2H_4 influences the exfoliation of $TiSe_2$, we perform DFT simulations on $TiSe_2$, Cu_xTiSe_2 systems and their interaction with N_2H_4. The calculations were performed with the Quantum Espresso software package using the Perdew–Burke–Ernzerho (PBE) functionals within the conjugate gradient approximation (GGA) and with PAW Pseudopotentials. In addition to analyzing the electrical and structural properties at the atomic level, we perform nudged elastic band (NEB) calculations were performed to study the activation energy for the diffusion of Cu adsorbed on $TiSe_2$. Our results, consistent with those previously reported [1], reveal a favorable interaction between the N atoms of N_2H_4 and the Se atoms in $TiSe_2$. We also observed that the intercalation of N_2H_4 increases the separation between the $TiSe_2$ sheets, which decreases the van der Waals interaction between them and facilitates the exfoliation process in the 3D material. These effects are enhanced by the presence of copper in the Cu_xTiSe_2 structure, since N_2H_4 also interacts favorably with Cu atoms. NEB calculations provide crucial information on the dynamics and mobility of Cu atoms in the material, contributing to a deeper understanding of doping transport and diffusion mechanisms.

REFERENCES

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