Magnetism in 2D van der Waals halide VI₃

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Abstract: Magnetic van der Waals (vdW) materials composed of two-dimensional (2D) layers bonded to one another through weak interactions exhibit promising potentials for high-tech magnetic, magnetoelectric, and magneto-optic applications in nanostructures. Due to their intrinsic magnetocrystalline anisotropy, several vdW materials could be thinned down to nanoscale thickness, while still maintaining magnetism. Prominent examples of such materials are transition metal trihalides, in particular CrI₃, a first atomically thin ferromagnet, realized in 2017.

Recently, VI₃ has been found to belong among 2D ferromagnets at temperatures below 50K. It is a semiconductor undergoing a subtle structural phase transition at 78K. Furthermore, its magnetic anisotropy exhibits rather unusual features. We have studied its properties by first principles calculations and reproduced the unusual magnetic anisotropy. Its properties have been linked to lattice distortions present at some of its low temperature phases.

Keywords: NANOMATERIALS, 2D MAGNETISM, VAN DER WAALS SYSTEMS, FIRST PRINCIPLES CALCULATIONS

1. Introduction

Van der Waals (vdW) crystals are fascinating materials with physical properties tuneable by varying the material thickness. Such lattice arrangement is predestined to exhibit complex magnetic structures with strongly anisotropic behaviour [1]. The early works in this field have mainly focused on creating of magnetism in nonmagnetic 2D materials through various approaches, including defect implementation, surface functionalization, and doping control. In contrast, in vdw halides of the compositions MX₂ where M is a transition metal cation and X is a halogen anion, magnetism is naturally incorporated by choosing a transition metal with a partially filled d-shell [2]. Up to only 3 years ago the possibility to create a monolayer 2D ferromagnet with nanoscale thickness was doubted, until first such case was discovered in a vdw halide CrI₃ [3]. The key to this success was its intrinsic magnetocrystalline anisotropy. The fundamental benefit is the richness of the transition metal halides family in which low dimensional magnetism can be examined and systematically investigated theoretically.

The possible appearance of ferromagnetism in 2D materials as well as their rich electrical and optical properties create opportunities not only for applications but for fundamental science discoveries like low-temperature quantum phenomena [4]. Current vdw materials exhibit various exotic physical properties, such as enhanced direct-gap semiconductors in monolayer MoS₂, Ising superconductivity in ion-gated superconductivity MoS₂ and atomic layer NbSe₂, robust in-plane ferroelectricity in atomic-thick SnTe, and complex magnetic interactions [5]. Mermin-Wagner theorem shows that the long-range 2D magnetic order is strongly suppressed above zero temperature for the isotropic Heisenberg model because the fluctuation is so strong that it destroys the spontaneous symmetry breaking immediately. But when magnetic anisotropy is included, the 2D ferromagnetism can be stabilized. It has just recently been realized in monolayer CrₓGe₂Te₅ [5] and CrI₃ [3].

Let us note that in the case of CrI₃, the t₂g triplet is fully occupied and orbital momentum is quenched. Therefore it is interesting to replace Cr by V having one electron less. Bulk VI₃ single crystals have been prepared recently. Information about the crystal structure at low temperatures has been contradictory in the beginning. The observed structures included trigonal R3 [6](similarly to CrI₃), C2/c [7], while other works reported inconclusive data [8]. After a significant experimental work it was concluded that the system orders in the trigonal R3 structure above the temperature Ts * [9]. At this temperature the system undergoes a monoclinic distortion. However, parameters of the monoclinic phase differ only slightly from the R3 phase and they are therefore difficult to distinguish. Another structure transition takes place at 32 K [9], this time into a triclinic variant whose parameters are not known yet.

By applying hydrostatic pressure, the ferromagnetic transition moves to higher temperatures up to 99 K at 7.3 GPa. In contrast, the low-temperature bulk magnetization is significantly reduced by applying pressure (by more than 50% at 2.5 GPa) suggesting a possible pressure-induced reduction of vanadium magnetic moment [10].

Existing theoretical works predict magnetic anisotropy with a strong uniaxial component corresponding to the out-of-plane easy magnetization axis for VI₃ [11], similarly to the case of CrI₃ [12]. These studies have however assumed always the more simple R3 structure. Current experiments predict perpendicular-to-plane easy axis (c axis) in works where only perpendicular and in-plane magnetizations were considered [7]. Studies of full angular dependence have shown a more unusual picture of MAE [13,14] with easy axis tilted about 40 deg from the c axis. In order to explain this discrepancy between experiment and theory we have examined whether the predicted easy axis direction is affected by the monoclinic distortion described above.

2. Results

Deeper understanding of the measured results is possible due to first principles calculation methods. Therefore the problem has been studied by the density functional theory (DFT) calculations employing the local spin-density approximation (LSDA), based on the full-potential linear augmented plane wave (FP-LAPW) method, as implemented in the band structure program ELK [15]. Spin-orbit coupling has been included in the calculation. The full Brillouin zone has been sampled by about 8000 k-points. For magnetic anisotropy calculations an increased accuracy of expansion into spherical harmonics has been used with lmax=14. Initial calculations were performed for the R3 structure. Since there were already indications that the material is a Mott insulator, we have also studied the effect of electron-electron correlations included in terms of the Hubbard correction term U acting on 3d electrons of V. In Figs. 1-2 we present densities of states for the cases with U = 0 and U = 3.8 eV, respectively. Notably the presence of U leads to opening of a gap between the conduction and valence band with a magnitude about 0.6 eV. Similar behavior can be seen in band structures (Figs. 3-4). Note the rather flat separated bands above the Fermi level (Fig. 4), which correspond to minority spin e states. Since our aim was to study the effect of distortion, the modified structure has been included approximately in a repeated calculation. This does not lead to a significant change of the DOS visible by eye.
In order to study magnetic anisotropy we calculated total energies of the structure for different tilting angles $\Theta$ from the c axis. These steps were performed for both the $R3$ structure and the distorted monoclinic structure. The energy as a function of the tilting energy is shown in Fig. 5 and is affected strongly by the distortion. Magnetic anisotropy energy for the distorted structure exhibits a deviation for angles between 30 and 40 deg, where a new minimum is established, in agreement with experimental findings.

In summary, our calculation methods have shown that the easy axis of V13 is indeed tilted by about 40 deg from the c axis as long as the monoclinic distortion of the lattice is taken into account.

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3. References

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