Electronic and magnetic properties of VOCl/FeOCl antiferromagnetic heterobilayers

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Abstract

We study the electronic properties of the heterobilayer of vanadium and iron oxychlorides, VOCl and FeOCl, two layered air stable van der Waals insulating oxides with different types of antiferromagnetic order in bulk: VOCl monolayers are ferromagnetic (FM) whereas the FeOCl monolayers are antiferromagnetic (AF). We use density functional theory calculations, with Hubbard correction that is found to be needed to describe correctly the insulating nature of these compounds. We compute the magnetic anisotropy and propose a spin model Hamiltonian. Our calculations show that interlayer coupling is weak and hence the magnetic order of each monolayers is preserved in the heterobilayer. Thus, the heterobilayer combines antiferromagnetic and ferromagnetic orders. Interlayer exchange should lead both to exchange bias and to the emergence of hybrid collective modes that combine FM and AF magnons. The energy band of the heterobilayer show a type II band alignment, and feature spin-splitting of the states of the AF layer due to the breaking of the inversion symmetry.

1. Introduction

The observation of magnetic order in stand-alone monolayers [1–3] derived from van der Waals layered magnetic compounds has started a new research area in 2D materials with potential for applications in spintronics [4]. Magnetic 2D crystals have also non-trivial physical properties such as topological magnons [5, 6], skyrmions [7], or quantized anomalous Hall effect [8, 9]. Moreover, the study of van der Waals heterostructures combining magnetic and non magnetic materials [10], as well as different types of magnetic materials, creates a huge space of opportunities to create artificial structures with novel properties [11]. This includes functional devices, such as spin filter tunnel junctions [12], as well as heterostructures where magnetic proximity effect promotes spin splitting in otherwise non-magnetic materials [10] as well as the emergence of topological superconductivity [11].

Here we choose to study heterobilayers made of two magnetic oxides like vanadium and iron oxychloride (VOCl [13–16] and FeOCl [17, 18]). Bulk FeOCl undergoes a paramagnetic to antiferromagnetic transition at 92 ± 3 K, according to Mossbauer spectra [19] with antiferromagnetic order in the monolayers. In contrast, neutron scattering experiments [14, 20] shows that bulk VOCl is formed by antiferromagnetically coupled monolayers with ferromagnetic order, very much like CrCl3 [21]. The Neel temperature of VOCl was reported to be 80 K [14, 20]. Recently, the ferrimagnetic phase of VOCl was reported at 150 K [22]. Importantly, both FeOCl [23] and VOCl [24] are insulating.

Moreover, FeOCl has a unique catalytic structure [25] and VOCl has potential as electrode material in rechargeable lithium-ion batteries [26, 27]. Theoretical studies have demonstrated that the bulk VOCl system has a strong magnetoelastic coupling that
might be used for development of magnetoelectric sensors and actuators [14].

Apart of the current applications, our initial motivation to look into VOCl and FeOCl comes from the fact that degradation of samples exposed to air has been a practical obstacle in the experimental research on most magnetic 2D crystals. In principle, we expect that magnetic oxides are not affected by this problem, showing good air stability in recent studies [22]. In addition, most of the work so far has focused on ferromagnetic compounds, with the notable exception of MPS$_3$ (M = Mn, Fe, Ni) [28].

Another reason to study these compounds comes from their lattice structure. The magnetic atoms in FeOCl and VOCl form a square lattice, different from the honeycomb lattices of the chromium trihalides [29] or FePS$_3$ [1, 2]. This may bring new possibilities in the study of moire magnets [30] or in the study of proximity effects [31].

In this work, we address the electronic and magnetic properties of van der Waals heterobilayers made of monolayers of FeOCl and VOCl. We explore emergent properties in the composite system that are missing in the constituent layers. We find that ferromagnetic (antiferromagnetic) order is preserved in the VOCl (FeOCl) monolayers, both on their own and forming part of a heterobilayer. We also report a type-II band alignment, useful for hosting long-lifetime excitons [32], and a spin splitting of the otherwise spin degenerate bands of FeOCl in the range of 2 meV.

The manuscript is organized as follows. In section 2, we briefly describe the application of density functional theory (DFT) together with the Hubbard correction to obtain the main properties of monolayers and FeOCl/VOCl bilayers. In section 3, we present our results for the monolayers and compare with the existing literature. In section 4, we present the results for the heterobilayer. In section 5, we present our conclusions.

2. Methods

We apply DFT [33], within the generalized gradient approximation (GGA), Perdew–Burke–Ernzerhof (PBE) parameterization [34], and the projector augmented-wave (PAW) method, including spin-orbit coupling, as implemented in the Vienna ab initio simulation package (VASP) [35, 36]. The electronic correlation of the d orbitals of Fe and V is computed with the Hubbard correction with values of 5.3 and 2.0 eV for d orbitals of Fe and V, respectively [37, 38]. In heterobilayers, the van der Waals interaction is accounted with the DFT-D3 method [39].

The lattice constants and internal coordinates are optimized until the residual forces on each atom are less than 0.01 eV Å$^{-1}$ and the energy convergence threshold is $10^{-5}$ eV. We have optimized using GGA+$U$. For all systems, a basis-set cutoff energy of 520 eV is used, and the sampling of the Brillouin zone (BZ) is a $10 \times 8 \times 1$ k-grid. A vacuum layer of 20 Å is set in the out-of-plane direction to avoid unphysical interactions between periodic replicas.

The crystal structure of monolayer FeOCl and VOCl, together with the FeOCl/VOCl heterobilayer is shown in figure 1. The space group for monolayers is $D_{2h}$ and the point symmetry is $C_{2v}$. In the case of the heterobilayer, the in-plane parameters are $a = 3.281$ Å, $b = 3.836$ Å for FeOCl and $a = 3.341$ Å, $b = 3.843$ Å for VOCl. In the case of the heterobilayer, the in-plane parameters are $a = 3.311$ Å, $b = 3.840$ Å, while the interlayer separation is $d = 2.66$ Å, as indicated in figure 1. The results of the structural optimization are in good agreement with previous works [19, 40, 41]. It is worth to mention that the strain of VOCl in the heterobilayer is smaller than 1% and it is not enough to turn the magnetic order to antiferromagnetic as reported for monolayer CrI$_3$ [42].

3. Electronic and magnetic properties of monolayers

3.1. Ab initio calculations

Based on a simple analysis of the chemical valence of the atoms in both compounds, we expect that both Fe and V are in the +3 oxidation state assuming that O and Cl have valence $–2$ and $–1$, respectively. In the case of FeOCl, the external shell of Fe$^{3+}$ is $3d^5$ and in the ionic limit relevant for an insulator, first Hund’s rule predicts a spin $S_{Fe} = 5/2$, and thereby a magnetic moment $M_{Fe} = 5\mu_B$. Our calculations give $M_{Fe} = 4.8\mu_B$, not far from the naive ionic picture. We have also found some residual magnetization of O and Cl atoms. Analogously, for VOCl the external shell of V$^{3+}$ is $3d^2$, and we expect an atomic spin $S_{V} = 1$, and a magnetic moment $M_{V} = 2\mu_B$. In our calculations we found $M_{V} = 1.7\mu_B$, in line with the results for FeOCl.

From the ionic picture, V and Fe are not closed shell. Therefore, an important question is whether the
3$d$ electrons form itinerant bands or, on the contrary, a bandgap opens in the bands calculated with DFT. This could happen due to several mechanisms. For instance, splitting of the half-full 3$d$ levels of Fe could open up a gap if exchange is larger than the bandwidth. Alternatively, crystal field of VOCl, whose 3$d$ shell is not half full, may lead to an orbital splitting, as it happens in CrI$_3$[43]. On the contrary, we find that, in our DFT calculations a bandgap only opens in FeOCl and VOCl monolayers when the Hubbard $U$ is included in the calculations, both when considering ferromagnetic (FM) and antiferromagnetic (AF) order on the layers. As we discuss below, we find that FeOCl monolayers are AF whereas VOCl monolayers are FM.

Regarding the electronic bandgap, in both semiconductors the bandgap is indirect. Nevertheless, in VOCl the conduction band (CB) minima is very close to the high symmetry point S, in which yields the valence band (VB) maxima. Considering the relative flat bands at VB and CB edges, the absorption/emission should be still comparable to that of direct 2D materials.

Figure 2 shows the band structures of FeOCl and VOCl monolayers computed with PBE+$U$ in the AF and FM phase, respectively, together with the projected DOS. In the case of FeOCl the hybridization of Fe $d$ orbitals with the Cl and O atomic orbitals is very strong, as shown in the projected DOS of the valence band. Note that the bottom of the conduction band is purely composed by iron. Moreover, the bands of FeOCl are doubly degenerate as expected on an antiferromagnet with an inversion center. In the case of VOCl the situation is pretty different, for two reasons: first, hybridization with O and Cl in both valence and conduction bands is very weak. Second, both valence and conduction band are spin polarized, with spin projection along the majority spin direction. We note that the top of the valence band of VOCl has a two-fold orbital degeneracy along the $SY$ and $SX$ directions.

In order to determine both the type of magnetic order and the magnetic anisotropy, we have carried out PBE+$U$ calculations considering both FM and AF configurations with spin pointing along four directions [001], [010], [001], and [110]. A summary of the ground state energies for different configurations is shown in table 1. Our PBE+$U$ calculations show that the AF and FM spin configurations are the stable phases for FeOCl and VOCl monolayer, respectively, in agreement with previous works [13, 44, 45]. In both compounds the ground states magnetization is lying along the $\{010\}$ axis, the spin points along the $\mathrm{V-O}/\mathrm{Fe-O}$ bond direction, projected along the plane of the layer.

### 3.2. Spin model

Given the insulating nature of the monolayers, we propose a spin model to describe the DFT calculations. The model has three types of terms, first-neighbour isotropic Heisenberg exchange, first-neighbour anisotropic exchange ($ae$) and single ion anisotropy ($sia$):

$$H = H_{\text{Heis}} + H_{ae} + H_{sia},$$

where:

$$H_{\text{Heis}} = \sum_{i,i'} S(i) \cdot S(i'),$$

$$H_{ae} = \frac{J_z}{2} \sum_{i,i'} S_z(i)S_z(i') + \frac{J_z}{2} \sum_{i,i'} S_x(i)S_x(i'),$$

and:

$$H_{sia} = \sum_i (E(S_x(i)^2) - S_z(i)^2) - DS_y(i)^2).$$

In the sums above $i$ runs over all the lattice sites of a square lattice and $i'$ runs over the four first neighbours of $i$. The first term accounts for first-neighbour isotropic exchange and the third term accounts for single ion anisotropy that reflects the symmetry of the crystal field of Fe and V atoms. In total, we have five parameters $J, E, D, J_y, J_z$. We estimate them using six DFT calculations (see appendix) and then we test the model with the remaining two. The results of the fitting gives an error with respect the DFT calculations of 7.95% and 6.09% for FeOCl and VOCl, respectively, which is rather satisfactory.

In both cases the single ion anisotropies $D, E$ are larger than the anisotropic exchange constants $J_y, J_z$. However, this difference is much smaller in the case of FeOCl. The smaller single ion anisotropy values in this case are probably due to the fact that the $d$ shell is half full for Fe, so that the orbital momentum is 0, even without crystal field quenching. The preponderance of single ion anisotropies, in both cases, is to be expected on account of the smaller atomic weight of the ligands, and thereby smaller spin–orbit coupling. We also note that the proposed model has...
two main limitations: it only considers first neighbour exchange and it completely ignores magnetoelastic interactions, that are known to be important for VOCl [14].

We now estimate $T_c$ for the VOCl monolayer. For that matter we follow the method of Torelli and Olsen [46], where an interpolation formula is proposed in order to account both for the spin wave fluctuations and the Ising-type fluctuations for a spin model simpler than ours, where only $D$ type single ion anisotropy is included. The interpolation formula is $k_B T_c = k_B T_0 \cdot \text{magn}(x)$, where $x = D / J$ and $\text{magn}(x) = \text{tanh}^{1/4} \log \frac{1}{1 + \gamma x}$, where $\gamma = 0.033$ and $z = 4$ is the number of first neighbours. With our parameters we find $k_B T_0 \text{magn} = 158$ K and $k_B T_c = 45$ K with such interpolation formula. The experimental values for bulk are in the 80 K range [14, 20], although a larger value has been recently reported [22]. In the case of FeOCl the anisotropy energies are much smaller. The mean field $T_c$, given by $k_B T_c = \frac{J S^2}{3}$, with $z = 4$ for the monolayer, yields 135 K, to be compared with the 92 K measured in bulk. Of course, mean field formula is a very rough estimate in 2D materials, since it ignores magnon fluctuations.

### 4. Electronic and magnetic properties of heterobilayers

We now address the electronic and magnetic properties of the VOCl/FeOCl heterobilayer. We assume the bulk stacking configuration for the heterobilayer, as shown in figure 1(c). As in the case of monolayers, we have explored several magnetic states. We consistently found that both the magnetic order type and the easy axis of the monolayers is preserved in the heterostructure. This indicates that interlayer exchange is weaker than both the intralayer exchange and the magnetic anisotropy.

The isolated FeOCl has two equivalent Néel states, that are related by time-reversal symmetry (inversion of the magnetization direction). Because of the buckling of the Fe atoms, interlayer exchange breaks this degeneracy, as one of the Fe magnetic sublattices is closer to the vanadium atoms than the other. We refer to these two phases as parallel (p) and anti-parallel (ap), for the FM and AF relative spin orientation of the two closest V-Fe atoms. Our calculations indicate that interlayer exchange is ferromagnetic. The difference of energy difference per unit cell, $\Delta E_{12}$ between the two states is related to the interatomic exchange as:

$$\Delta E_{12} = j S q S_{\text{Fe}},$$  \hspace{1cm} (5)

where $j$ is the interlayer exchange coupling. We are ignoring here the small anisotropy of this quantity, which is already small. Indeed, we have $\Delta E_{12} = 0.14$ meV from which we infer $j \approx 0.056$ meV. This interlayer exchange should lead to exchange bias of the hysteresis cycle of the VOCl monolayer as well as the splitting of the otherwise degenerate AF magnons of the FeOCl and very likely their hybridization, at finite $q$ with the FM magnons of the VOCl bilayer. This hybridization is expected because the AF magnons have a larger $q = 0$ magnon gap than the FM magnons but a smaller dispersion, on account of their linear dispersion. At the crossing point, interlayer exchange should lead to hybridization gap driven by the interlayer exchange. This will be the subject of future work.

We now discuss the electronic properties of the hetero-bilayer. Figure 3 shows the band structure and the projected DOS of the most stable magnetic state of the heterobilayer. The bilayer exhibits an indirect bandgap of 1.38 eV. From the projected DOS we determine that the band alignment is type II, similar to the case of heterostructures of transition metal dichalcogenides [32, 47]. The top of the VB is mainly composed by V orbitals while the bottom of the CB is dominated by the Fe wave functions. Interestingly, we

| Table 1. Magnetocrystalline anisotropy energies $E_{[001]} - E_{[010]}$, $E_{[001]} - E_{[100]}$, and $E_{[110]} - E_{[001]}$ (meV/unit cell). The reference is the total energy of the 010 direction, $E_{[001]}$, which in all cases is found to be the ground state. For the heterobilayer AF/Fe/FM(V)-p stands for parallel spin polarization of neighbor Fe and V atoms and AF/Fe/FM(V)-ap for anti-parallel spin polarization. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2D Crystal | GS | $E_{[100]}$ | $E_{[110]}$ | $E_{[001]}$ | $E_{[110]}$ |
| FeOCl | FM | 54.635 | 54.396 | 54.797 | 54.518 |
| VOCl | AF | 0.201 | 0 | 0.275 | 0.102 |
| VOCl/FeOCl | AF(Fe)/FM(V)-p | 0.585 | 0 | 1.614 | 0.340 |
| VOCl/FeOCl | AF(Fe)/FM(V)-ap | 0.733 | 0.140 | 1.750 | 0.482 |

| Table 2. Parameters of the spin model of monolayer FeOCl and VOCl, expressed in meV: The energy difference $\epsilon_{110} - \epsilon_{010}$ obtained from the model is the AF case for FeOCl and the FM case for VOCl. The error is $\Delta = \frac{|(\Delta_{\text{model}} - \Delta_{\text{DFT}})/(\Delta_{\text{model}} + \Delta_{\text{DFT}})|}{100}$. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| FeOCl | VOCl | $S$ | $J_f$ | $J_z$ | $D$ | $E$ | $\epsilon_{110} - \epsilon_{010}$ | $\Delta$ (%) |
| 5/2 | 1 | 2.177 meV | $-6.024$ meV | $-1.6$ $\mu$eV | $6.2$ $\mu$eV | $3.5$ $\mu$eV | $10.7$ $\mu$eV | $5.1$ $\mu$eV | $861.1$ $\mu$eV | $-9.5$ $\mu$eV | $430.7$ $\mu$eV | $0.1196$ meV | $0.2089$ meV | $7.95$ | $6.09$ |
find that both band extrema feature splittings missing in the monolayer. In the case of the CB, we find a spin-splitting of the Fe bands. This can arise either from the interlayer spin exchange or from the breaking of inversion symmetry of the heterobilayer. The fact that the sign of the splitting is the same for the two interlayer alignments, parallel and antiparallel, discussed above is a strong suggestion that the origin of the splitting is due to the absence of inversion symmetry [48]. On the other hand, the splitting observed in the top of the VB occurs between two states with the same spin and is related to reduced symmetry of the heterobilayer.

5. Conclusions

We have characterized the electronic and magnetic properties of VOCl/FeOCl heterobilayers using ab initio methods, including the electronic correlation effects within the framework of the Hubbard method. Consistent with experimental work, we find that VOCl (FeOCl) monolayers are ferromagnetic (antiferromagnetic) insulators with an easy axis along the [010] direction. We find a hybrid magnetic order for VOCl/FeOCl heterobilayers, that combines the ferromagnetism of the VOCl monolayer and the antiferromagnetic order in the FeOCl layer. Interlayer exchange is found to be ferromagnetic and should result in a bias of the hysteresis cycle of the VOCl monolayer. Moreover, the reduced symmetry of the heterobilayer causes a spin splitting of both conduction and valence band edges of \( \pm 2 \) meV. The heterobilayer has a type-II band alignment, with the conduction/valence band localized in the Fe(V) layer. Interestingly, combined with the spin splitting of the valence band states, interlayer excitons in this system would have a well-defined spin polarization. Therefore, the magnetic properties can be combined with a long lifetime for the excitons. We also foresee the emergence of hybrid magnon modes combining the AF and FM magnons of both layers.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Appendix. Determination of parameters of the spin model

The parameters \( J, J_z, J_y, D \) and \( E \) are calculated from the classical energies per atom:

\[
\epsilon_{\eta}(\vec{n}) \equiv \frac{E_{\eta=\pm 1}(\vec{n})}{N_{\text{at}}} = S^z \frac{\eta \varepsilon(J + J_n n_z^2 + J_y n_y^2)}{2} + S^2 \left( E(n_z^2 - n_y^2) - D n_z^2 \right),
\]  

where \( \eta = +1(-1) \) stands for FM (AF) configurations, \( S = 1, 5/2 \) is the spin of for V and Fe, respectively, \( z = 4 \) is the number of first neighbours, and \( \vec{n} = (n_x, n_y, n_z) \) is the unitary vector that marks the different orientations of the magnetic moments. The single ion magnetic anisotropy does not depend on \( \eta \). We obtain six configurations (FM and AF) for the three different orientations of the magnetic moments along the crystal axis:

\[
\epsilon_{\eta}(\vec{n}_x) \equiv \frac{E_{\eta=\pm 1}(\vec{n}_x)}{N_{\text{at}}} = S^z \frac{\eta \varepsilon(J + J_x n_x^2)}{2} + S^2 (E(n_x^2)),
\]

\[
\epsilon_{\eta}(\vec{n}_y) \equiv \frac{E_{\eta=\pm 1}(\vec{n}_y)}{N_{\text{at}}} = S^z \frac{\eta \varepsilon(J + J_y n_x^2)}{2} + S^2 (-D n_z^2),
\]

\[
\epsilon_{\eta}(\vec{n}_z) \equiv \frac{E_{\eta=\pm 1}(\vec{n}_z)}{N_{\text{at}}} = S^z \frac{\eta \varepsilon(J + J_z n_z^2)}{2} + S^2 E(-n_z^2).
\]
In order to derive $J$ we can use:

$$\epsilon_{FM}(100) - \epsilon_{AF}(100) = S^2 zJ.$$  \hspace{1cm} (A2)

We now can obtain $J_x$ and $J_y$ from

$$\epsilon_{FM}(010) - \epsilon_{AF}(010) = S^2 zJ_x + S^2 zJ_y$$  \hspace{1cm} (A3)

and

$$\epsilon_{FM}(001) - \epsilon_{AF}(001) = S^2 zJ_x + S^2 zJ_y.$$  \hspace{1cm} (A4)

In order to derive the single ion anisotropies, $E$ and $D$ we now compare FM energies along different directions:

$$\epsilon_{FM}(100) - \epsilon_{FM}(010) = DS^2 + ES^2 + \frac{J_x S^2}{2}$$  \hspace{1cm} (A5)

and

$$\epsilon_{FM}(001) - \epsilon_{FM}(010) = DS^2 - ES^2 + \frac{J_y S^2}{2} - \frac{J_z S^2}{2}$$  \hspace{1cm} (A6)

with two equations and two unknowns. Table 2 summarizes the parameters of monolayer FeOCl and VOCl obtained from the DFT values of table 1.

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