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A comparative study of structural, electronic and magnetic properties of DyOCl and HoOCl lanthanide oxychlorides: first-principles predictions of DFT, DFT + U and DFT + U + SOC methods

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Abstract

Apart from their fundamental interest, lanthanide compounds have potential implications as luminescent, catalytic, magnetic as well as biomedical materials for diverse applications. In this paper we report first time the electronic and magnetic properties of two members of lanthanide oxychloride family, namely: DyOCl and HoOCl from the first-principles calculations based on density functional theory (DFT). For the self-consistent DFT calculations, we incorporated the full-potential linearized augmented plane-wave (FP-LAPW) method using various DFT methods and DFT + U method without and with spin–orbit coupling (SOC). For the electronic structure calculations, the exchange-correlation energy functionals in Kohn–Sham equation are treated within local-spin-density-approximation (LSDA) and Generalized-Gradient-Approximation (GGA) in conjunction with Perdew–Bruke–Ernzerhof (PBE) and Wu-Cohen (WC) parameterization. In particular, a comparative analysis of electronic and magnetic properties is presented with LSDA, PBE-GGA, WC-GGA and GGA + U methods without and with SOC coupling. Both compounds are predicted to be half-metallic (HM) ferromagnetic (FM) within LSDA approximation, whereas within GGA + U approximation DoOCl is semiconducting while HoOCl is HMFM. On the other hand, the GGA + U scheme under FM and antiferromagnetic (AFM) ordering predicts that both DyOCl and HoOCl are metallic in AFM ordering while they show insulating nature in FM ordering.

1. Introduction

Lanthanide (Ln) compounds are of considerable interest owing to their unique electronic, optical, magnetic and catalytic properties [1]. For instance, Lanthanide Oxychlorides LnOCl (Ln = Dy, Ho) are used in advanced materials which are commercially reliable and also have a great interest in fluorescent materials [2]. These compounds are the major source of luminescent phosphors which are used in the production of optoelectronic and display devices [3–8]. The main reason for efficient luminescence of oxycompounds is the presence of rigid and stable structure of the formula unit (LnO)₅ⁿ⁺, which can withstand any phase transitions or lattice defects subjected to external influence which can affect the luminescence.

Owing to their peculiar behavior, the lanthanide compounds can be used in upconversion photoluminescence mechanism, thus simulating higher frequency photons from the lower frequency photons while exciting the materials. The fundamentally useful phenomenon of upconversion finds potential applications in solid-state devices such as laser, solar cells, display screens and biomedical image devices [6–13]. Mainly, the peculiar electronic and magnetic properties of Ln compounds owe to the localized nature of valence electrons of 4f orbitals. Despite the small overlapping of 4f orbitals of Ln elements with the interacting ligand orbitals, the energy of 4f orbitals is quite comparable with that of ligand orbitals which enhances the reactivity of Ln compounds [14]. Besides, owing to their peculiar physical, chemical and magnetic properties Ln complexes
have potential implications in biomedical field [15, 16]. Further, the variable coordination environment of Ln elements (having $4f^{n-14d^a-6s^c}$ valence electronic configuration), which in turn varies chemical bonding ability with ligands, plays a significant role to predict and formulate novel materials [16].

The aim of this paper is to report on the structural, electronic and magnetic properties of two important compounds of LnOCl family, namely- DyOCl and HoOCl from DFT first-principles calculations. In particular, it is important to investigate electronic and magnetic properties of lanthanides compounds which are less studied to explore their prospects for electronic, magnetic and biomedical applications. The motivation of the study arises from the lack of research on the aforementioned physical properties of the two oxychloride compounds under consideration. In particular, to our knowledge, so far no considerable work has been published on the DFT based first-principles simulations of DyOCl and HoOCl oxychlorides with the aforementioned methods. On the other hand, in past most of the work was focused on the experimental investigation of crystal structure and thermodynamic properties of rare-earth oxychlorides [1, 17–23], except with a few recent studies on experimental and theoretical investigation of electronic, magnetic and optical properties of oxyhalide compounds [17, 24, 25]. One reason for less search on LnOCl compounds is due to difficulty in making large-scale fine-crystal structure of many such compounds [17]. Moreover, there is a need to explore in detail the exact nature of energy band structure and magnetic behavior of the lanthanide oxyhalide compounds by incorporating both the Hubbard potential (to count for onsite Coulomb repulsion of localized 4f electrons of lanthanide species) and SOC coupling. The current study is an attempt towards the same.

The structure of LnOCl layered compounds can be perceived by a general formula (LnO)$_n$ $^n$Cl$^-$, which can be understood as distinct layers of covalent complex cations (LnO)$_n$ $^n$ and chloride anions Cl$^-$. They are inorganic compounds while most of them exit in PbFCl-type tetragonal crystalline shape and belong to spatial symmetry group $P4/nmm$ (Z = 2 and No = 129) [22]. Some heavier LnOCl compounds (e.g., HoOCl, ErOCl, TmOCl, and YbOCl), however, can crystallize in the hexagonal $R3$ m space group with SmSII and YOF mixtures 2-dimensional polymorphic structure [1]. The volume occupied by hexagonal geometry of LnOCl is much smaller than that of the tetragonal geometry. The SmSI crystal structure of LnOCl reveals that there are four oxygen and five chlorine atoms bonded with each Ln$^{3+}$ ion. The chemical structure of the layered LnOCl is considered a sequence of homoatomic layers, i.e. Cl-Ln-O-O-Ln-Cl [1, 17, 22]. Layered compounds have attracted immense interest more recently owing to their peculiar properties with diverse technological implications [24]. For various experimental procedures for the preparation of LnOCl crystalline structure, interested readers are referred to [17, 22, 25–29].

Dysprosium oxychloride DyOCl is an inorganic compound with a very rigid and stable unit structure of (DyO)$_n$ $^n$, thus leading to efficient luminescence [22]. The structural data for DyOCl is incoherent and inconsistent [25]. The sample of DyOCl structure can be studied by X-ray diffraction powder evaluation. Holmium oxychloride HoOCl is also an inorganic compound having similar formula unit. Different techniques, i.e. valence bond calculations, analysis of Rietveld and X-ray diffraction of powder measurements have been employed for studying the crystal structure of HoOCl. Rietveld analysis revealed micro absorption effects with a list of coherent structural constants [25].

### 2. Theory and methodology

We have invoked DFT formulation for calculating the structural, electronic and magnetic properties of DyOCl and HoOCl compounds within various exchange-correlation energy functionals. For the first-principles DFT calculations, we have incorporated FP-LAPW method as implemented in WIEN2k [30]. For the calculation of ground state electronic structure of the compounds, we employed various approximated potentials for the exchange-correlation terms in Kohn–Sham equation (KSE), namely- L(S)DA [31], GGA [32], WC-GGA [33], PBE-GGA [34] and GGA + U methods both for majority spin (spin-up) and minority spin (spin-down) polarization modes. For the electronic and magnetic properties we have also incorporated SOC coupling both in FM and AFM ground state phases.

In order to obtain the optimized stable crystal structure, we first computed the total energy $E$ of the compounds at various volumes by relaxing the geometrical parameters of the crystal structure. For the computation of the Bulk modulus $B_0$ and its pressure derivative $B'_0 = dB_0/dP$ by fitting ground state energy $E_0$ into the Murnaghan’s equation of state [35],

$$E(V) = E_0 + \frac{9V_0 B_0}{16} \left(\left\{\frac{V_0}{V}\right\}^\frac{3}{2} - 1\right)^2 B'_0 + \left\{\left(\frac{V_0}{V}\right)^\frac{3}{2} - 1\right\} \left\{6, -4, \left(\frac{V_0}{V}\right)^\frac{3}{2}\right\}$$

In the procedural methodology of all-electron FP-LAPW, the k-space is partitioned into the interstitial region (IR) and non-interstitial non-overlapping spheres, called the muffin tin (MT) spheres having centre at the
atomic positions. In the former region of space, the basis vectors in the form of Kohn–Sham–orbitals (KSO) are assumed to be plane waves representing freely moving electrons, whereas in the later region the basis vectors representing the bound core electrons are assumed to be spherical harmonics. For the convergence of self-consistent calculations, the k-points mesh of 18 000 for the compounds was selected. Besides, for integration procedure in the irreducible Brillouin zone the total energy of crystal was set not to exceed 0.1 mRy. The plane wave expansion in terms of KSO is made under the condition $R_{MT} \times K_{\text{max}} = 6$, where $R_{MT}$ is minima of the atomic-sphere radius and $K_{\text{max}}$ is the maximum value of the interstitial plane wave vector in the expansion.

3. Results and discussion

3.1. Structural properties

Stability of crystal structure for LnOCl at ambient conditions subjected to various temperature and pressure is of great interest [7, 8, 19]. The results of volume versus energy curve (not shown) revealed that both DyOCl and HoOCl are stable for spin polarization calculations without and with SOC coupling both in FM and AFM ordering. Optimized equilibrium lattice parameters of DyOCl and HoOCl were used to find the electronic crystal structure by optimizing the total energy of the compounds.

The comparison of computed optimized lattice parameters with experimental data from the results of X-ray diffraction of powder of DyOCl and HoOCl crystal structures, obtained from Rietveld refinement data, is given in tables 1—4. The calculated values are rounded off to three decimal places where applicable. As can be seen, the computed lattice constants by PBE-GGA are more close to experimental results, except with little overestimation of c. There is a slight difference between experimental and our computed calculations which may be due to non-interacting nature of DFT potential; the same can be noted, in particular, for the low values of computed lattice parameters against LDA. It is because LDA, in contrast to GGA and other variants of DFT exchange-correlation potential, is based on noninteracting system of particles. In addition, bulk modulus, ground state energies and pressure derivative of bulk moduli are also computed which do not exist in the corresponding references.

For DyOCl the PBE-GGA method calculates the ground state energy of the order $-50\,820.519$ Ry while with GGA + U method the calculated ground state energy is of the order $-50\,821.508$ Ry and hence predicts more stability in the ground state. Similarly for HoCl the method GGA + U predicts more stable structure with calculated ground state energy $-52\,661.899$ Ry in contrast to PBE-GGA method with calculated value of energy $-52\,661.112$ Ry. With GGA + U method in FM order including SOC coupling the ground state energy for DyOCl is $-50\,821.507$ Ry. While in the AFM ordering DyOCl is more stable with ground state energy $-101\,643.314$ Ry. On the other hand in case of HoCl the GGA + U method predicts more stability in AFM ordering with the ground state energy $-105\,324.681$ Ry in contrast to the calculated energy $-52\,662.210$ Ry with GGA + U method in FM order including SOC coupling.

3.1.1. Electronic properties

In this section we present electronic properties of DyOCl and HoOCl lanthanide compounds by calculating orbitals projected density of states (PDOS), total density of states (TDOs) and energy band structure (EBS) with LSDA and GGA + U methods without SOC coupling and magnetic ordering (MO) as well as with GGA + U incorporating SOC coupling in FM and AFM ordering. The computed electronic band structure of DyOCl within simple LSDA method is shown in figure 1. As can be seen, energy band gap with spin up states (figure 1(a)) is direct in nature for both spin states at point $\Gamma$ of Brillouin zone with a wide band gap of 5.24 eV, rendering DyOCl insulator in nature. For spin down channel (figure 1(b)), the Fermi level is surrounded by a cluster of valence orbitals of Dy 4f electrons while for spin up case cluster of Dy 4f orbitals appears around $-4$ eV. As such DyOCl is HMFHM in nature, this property can be used in various applications in spintronic and spinpolarized devices.

The behavior of band structure results from various orbitals contributions as can be seen from plots of total and partial density of states shown in figure 2. In fact, densities of states describe the electronic states which are occupied by the electrons per unit volume within certain energy range. We can calculate different properties of solid materials like optical, electronic and magnetic by using electronic densities of states.

Electronic band structure of HoOCl computed by LSDA approximated potential is shown in figure 3. Analogous to DyOCl, a wide direct band gap for HoOCl with spin–up having value of 5.37 eV is calculated. While for spin–down, zero band gap is calculated. This in turn implies that HoOCl is also HMFHM in nature.

Overall trend in energy band structure is same as discussed earlier in case of DyOCl. The plots of density of states (not shown) were also identical to that of DyOCl.

For comparison sake, we have also calculated EBS of DyOCl with simple GGA + U method which is shown in figure 4. The asymmetry of band gap between the two spin polarized states implies that DyOCl is half-metallic in nature in contrast to semiconductor nature of CeOCl predicted earlier [17] from first-principles calculations at
Hubbard potential $U$ value of 4.8 eV. However, the same study [17] predicted metallic behavior of DyOCl with $U$ values less than 4.5 eV. On the other hand, in our case, after applying $U$ potential of order 7 eV on 4f electrons of Dy within GGA + $U$ scheme, the modified energy band structure rendered DyOCl to behave as insulator as shown in figure 4. The insulating behavior is consistent with results of series of lanthanide oxyhalides LnOX (Ln = La, Lu; X = Cl, Br, I) presented in [26] carried out with Tran–Blaha modified Becke–Johnson potential (TB-mBJ).

Although, average energy band gap for spin up case is invariant under GGA + $U$ operation, however, the part of valence band which was earlier lying at some distance below the Fermi level is shifted upwards to the Fermi level while the conduction band is also shifted above 4 eV in a smooth way. Similarly, for spin down case, the Dy 4f orbitals are merged into the valence band after a little downwards shift from their earlier position above the Fermi level. Thus, the implementation of Hubbard potential within GGA method has improved the energy band structure by taking into account the onsite Coulomb repulsion arising from Dy 4f electrons. Our choice of GGA + $U$ method over the LDA + $U$ method for the electronic properties is due to the fact that LDA + $U$ only slightly changed the energy band as predicted by Chaudhary et al [37] for a series of compounds.

| Table 1. Comparison of computed lattice parameters (with no spin) with experimental data for DyOCl. |
|---------------------------------------------------------------|
| **Unit cell parameters (Å)** | **PBE-GGA** | **WC-GGA** | **LDA** | **Experimental values** |
| a = b | 3.887 | 3.809 | 3.769 | 3.908 [18], 3.911 [22], 3.911 [36], 6.615 [18], 6.63 [22], 6.620 [36] |
| c | 6.711 | 6.644 | 6.485 | 101.00 [18], 101.26 [36] |
| Ground state volume ($Å^3$) | 101.419 | 96.405 | 92.136 | 101.00 [18], 101.26 [36] |
| Bulk modulus B(GPA) | 95.826 | 95.826 | 122.772 |
| $B' = dB/dP$ | 4.838 | 4.838 | 4.616 |

| Table 2. Comparison of computed lattice parameters (with spin) with experimental data for DyOCl. |
|---------------------------------------------------------------|
| **Unit cell parameters (Å)** | **PBE-GGA** | **WC-GGA** | **LDA** | **Experimental values** |
| a = b | 3.897 | 3.812 | 3.745 | 3.908 [18], 3.911 [22], 3.911 [36], 6.615 [18], 6.625 [22], 6.620 [36] |
| c | 6.692 | 6.661 | 6.646 | 101.00 [18], 101.26 [36] |
| Ground state volume ($Å^3$) | 101.647 | 96.801 | 93.230 | 101.00 [18], 101.26 [36] |
| Bulk modulus B(GPA) | 95.432 | 111.629 | 130.684 |
| $B' = dB/dP$ | 5.414 | 4.716 | 5.420 |

| Table 3. Comparison of computed lattice parameters (with spin) with experimental data for HoOCl. |
|---------------------------------------------------------------|
| **Unit cell parameters (Å)** | **PBE-GGA** | **WC-GGA** | **LDA** | **Experimental values** |
| a = b | 3.918 | 3.847 | 3.782 | 3.890 [18], 3.895 [36] |
| c | 6.668 | 6.602 | 6.578 | 6.695 [18], 6.602 [36] |
| Ground state volume ($Å^3$) | 102.136 | 97.724 | 94.099 | 99.82 [18], 100.06 [36] |
| Bulk modulus B(GPA) | 102.136 | 115.807 | 127.950 |
| $B' = dB/dP$ | 4.579 | 4.647 | 4.452 |

| Table 4. Comparison of computed lattice parameters (with no spin) with experimental data for HoOCl. |
|---------------------------------------------------------------|
| **Unit cell parameters (Å)** | **PBE-GGA** | **WC-GGA** | **LDA** | **Experimental values** |
| a = b | 3.941 | 3.866 | 3.800 | 3.890 [18], 3.895 [36] |
| c | 6.692 | 6.624 | 6.635 | 6.695 [18], 6.602 [36] |
| Ground state volume ($Å^3$) | 103.918 | 99.016 | 95.784 | 99.82 [18], 100.06 [36] |
| Bulk modulus B(GPA) | 104.234 | 117.573 | 132.548 |
| $B' = dB/dP$ | 4.568 | 5.038 | 4.669 |
The energy band structure of HoOCl with GGA + U potential is shown in figure 5. Interestingly, here, again metallic nature of HoOCl compound can be seen from the overlapping of valence and conduction band around the Fermi level in spin up configuration. In the case of spin down polarization, however, there is a wide

![Figure 1. Energy band spectrum of DyOCl with LSDA potential for (a) spin up and (b) spin down.](image)

![Figure 2. Plots of TDOS and PDOS of DyOCl for both spin up and spin down states. Where, (a) is for TDOS of DyOCl, (b) is for PDOS of Dy, (c) is for PDOS of O, (d) is for PDOS of Cl.](image)
band gap of order 5.6 eV at \( \Gamma \). The plots of TDOS and PDOS for both DyOCl and HoOCl with GGA + \( U \) method are shown in figures 6(a)–(d). As is obvious there is a large asymmetry between density of states for spin up and spin down polarization states. For comparison, the computed TDOS of HoOCl for spin up and spin down states are also shown in figure 6(a) with LSDA functional.

Finally, we present the results by implemented the SOC coupling and MO ordering within GGA + \( U \) method. The resulting energy band structure and plots for density of states are shown in figures 7–9. Interestingly, for FM ordering DyOCl shows insulating nature (figure 7(a)) while it is metallic in AFM ordering...
Figure 5. Energy band spectrum of HoOCl with GGA + U method for (a) spin up and (b) spin down.

Figure 6. Plots of TDOS and PDOS for both spin up and spin down states. Where, (a) is for TDOS of HyOCl with LSDA; (b) is for TDOS of HoOCl with GGA + U; (c) is for PDOS of HoOCl with GGA + U; (d) is for PDOS of DyOCl with GGA + U.
Similar trend in the EBS for HoOCl is noticed as shown in figure 8. This is in contrast to the half-metallic nature of both compounds predicted earlier with LSDA method (figure 1). It should also be noted that this behavior is different from the one obtained with GGA+U method where DyOCl shows semiconducting nature while HoOCl shows half-metallic nature as was shown in figures 3-4. From this one may conclude that for these lanthanide compounds GGA+U method seems to be more accurate than GGA+U+SOC scheme which simply restores the LSDA character. However, this is not strictly true for the calculated magnetic moments (table 7). On one hand results of PBE-GGA, GGA+U and GGA+U+SOC methods in FM ordering for DyOCl give magnetic moment of order 10.00 $\mu_B$ which is consistent with experimental value.

*Figure 7.* Energy band spectrum of DyOCl using GGA+U method with SOC and MO; where (a) spin up for FM and (b) for AFM.

*Figure 8.* Energy band spectrum of HoOCl using GGA+U method with SOC and MO; where (a) is for spin up in FM and (b) is for spin down in AFM ordering.
10.60 \( \mu_B \) [1], on the other hand for HOCl the magnetic moment of the order 8.00 \( \mu_B \) calculated for GGA + U and GGA + U + SOC differs largely from the experimental value of 10.46 \( \mu_B \) [22] than 10.00 \( \mu_B \) which has been calculated by LSDA, PBE-GGA and GGA + U + SOC methods in FM ordering. From this, it is reasonable to conclude that the different magnetic behavior of DyOCl and HoOCl for same exchange-correlation functionals may be due to different interacting role of 4f orbitals of Dy\(^{3+}\) and Ho\(^{3+}\) with same ligants. In particular, among all trivalent rare-earth ions the 4f\(^6\) electron configuration of the Dy\(^{3+}\) ion renders it the most complex energy level structure [38].

### 3.1.2. Magnetic properties

At fundamental level, origin of magnetism in magnetic materials arises from the orbital and spin motion of nuclei and electrons. As nuclei are heavier so their motion in contrast to that of electrons is ignored in this regard. Mainly unpaired electrons constitute the spin magnetic moment of the magnetic materials. Sum of orbital and spin moments of closed shell electronic systems is zero. For diamagnetic materials, the opposite motion of paired electrons leads to zero magnetic moment. Paramagnetic materials, however, possess small nonzero magnetic moment induced from the dipole moments of unpaired electrons. In ferromagnetic materials, this effect is even more pronounced in which atomic dipole moments are aligned parallel to one another due to internal crystal field or equivalent exchange interaction in the absence of an applied field [39]. As, in contrast to magnetic moment of ferromagnetic materials, magnetic moments of diamagnetic and paramagnetic materials are small so they are called non-magnetic. The Hill theory [40], ascribes the magnetic fate of the materials to the near neighbor distance and hence the degree of delocalization of 5f electrons wave functions of adjacent actinides atoms.

The Hill’s criteria, nevertheless, usually fails in the species having f delocalized electrons which overlap with \( (p, d) \) states to form energy band structures. In many compounds, such as transition or inner transition (lanthanides) metal systems etc, the orbital angular momentum is quenched being strongly tied to a crystalline [19], hence for such systems to a good approximation we can take \( L = 0 \), and \( J = S \) [39]. The electronic structures of close-packed systems reveal sharp peaks in the density of states near the Fermi level, which cause strong magnetic effects. Magnetic behavior of the compounds under study is also reflected from the mirror asymmetry in DOS for majority and minority spin polarization sates.

### 3.1.3. Magnetic properties of DyOCl and HoOCl

The asymmetric Dy narrow bands below and at the Fermi level seem to mainly contribute to the spin magnetic moments of DyOCl and HoOCl. To our knowledge, spin magnetic moments of DyOCl and HoOCl compounds have been not investigated from first-principles calculations in the past. We have employed the optimized lattice parameters to calculate spin magnetic moments of DyOCl and HoOCl with various DFT exchange-energy functionals, which are given in tables 5–6. Besides, we have also computed magnetic properties with SOC coupling in the two MO regimes, i.e. FM and AFM as given in table 7. In case of DyOCl, total maximum calculated spin magnetic moment is 10.00 \( \mu_B \) for GGA + U method without and with SOC and FM ordering. On the other hand, the experimental value of total magnetic moment of DyOCl is 10.60 [1].

However, in case of HoOCl the calculated maximum spin magnetic moment is 10.00 \( \mu_B \) for PBE-GGA potential while it is 8.00 \( \mu_B \) for each LSDA and WC-GGA potential and GGA + U without and with SOC coupling in FM ordering. Whereas, the effective magnetic moment of HoOCl measured between temperature 100 and 300 K is 10.46 \( \mu_B \) [22]. The calculated integer values of spin magnetic moments per unit cell further confirm the half-metallic nature of DyOCl and HoOCl oxychlorides. The materials with half-metallic nature have attracted attention for potential applications in spintronics devices owing to their characteristic magnetic nature which arises from the asymmetry of spin polarized density of states [41].

The main contribution of spin magnetic moment in lanthanides compounds stems from the magnetic moment of lanthanide cations. For instance, magnetic moment of Dy\(^{3+}\) free ion is 10.65 \( \mu_B \) in contrast to its effective value of order 10.46 \( \mu_B \) for DyOCl [22]. On the other hand, the magnetic moment of element Dy at Curie temperature (88 K) is 10.2 \( \mu_B \) [39].

The effective values of spin magnetic moment calculated in these compounds are likely to be attributed to the presence of magnetic structures, which is also observed for some members of LnOCl [22]. This can be further justified by the localized orbitals of Dy\(^{3+}\) and Ho\(^{3+}\) ions at the Fermi level.

### 4. Conclusion

In this paper, we have reported a systematic analysis of structural, electronic and magnetic properties of two important members of lanthanide oxyhalide family, namely- DyOCl and HoOCl from first-principles DFT calculations, which are less studied for these properties. We employed all-electron full-potential method for the comparative analysis of structural properties using LDA, PBE-GGA, and WC-GGA DFT exchange correlation...
functionals both for spin-up and spin-down electronic polarization states. The optimized lattice constants calculated in our work with PBE-GGA approximation are nearly equal to the experimental lattice parameters. Besides, we have employed LSDA, GGA $+U$ method as well as GGA $+U +$ SOC scheme both in FM and AFM ordering.

Table 5. Computed magnetic moments (in $\mu_B$) for DyOCl compared with experimental data.

| Spin magnetic moments type | This work | Experimental value |
|---------------------------|-----------|--------------------|
|                           | LSDA      | PBE-GGA            | WC-GGA | GGA + $U$ | |
| Interstitial spin         | 0.192     | 0.282              | 0.189  | 0.093     | |
| In sphere 1(Dy)           | 3.636     | 4.681              | 3.665  | 4.978     | |
| In sphere2 (O)            | 0.221     | 0.157              | 0.205  | $-0.017$  | |
| In sphere3 (Cl)           | 0.047     | 0.021              | 0.035  | $-0.006$  | |
| Total spin magnetic moment in unit cell | 8.00 | 10.00 | 8.00 | 10.000 | 10.60 [1] |

Table 6. Computed magnetic moments (in $\mu_B$) for HoOCl compared with experimental data.

| Spin magnetic moment types | This work | Experimental value |
|----------------------------|-----------|--------------------|
|                            | LSDA      | PBE-GGA            | WC-GGA | GGA + $U$ | |
| In interstitial            | 0.286     | 0.282              | 0.283  | 0.049     | |
| In sphere 1(Dy)            | 4.663     | 4.681              | 4.680  | 3.898     | |
| In sphere2 (O)             | 0.163     | 0.157              | 0.156  | 0.076     | |
| In sphere3 (Cl)            | 0.031     | 0.021              | 0.023  | 0.002     | |
| Total spin magnetic moment in unit cell | 10.00 | 10.00 | 10.00 | 8.000 | 10.46 [22] |

Table 7. Calculated magnetic moments of DyOCl and HoOCl with GGA $+U$ method with SOC coupling in the FM and AFM ordering.

| Compound | Order | Spin magnetic moments type | Calculated values of spin magnetic moment |
|----------|-------|-----------------------------|------------------------------------------|
| DyOCl    | FM    | In interstitial             | 0.093                                    |
| Dy       |       | In sphere 1(Dy)             | 4.978                                    |
| O        |       | In sphere 2 (O)             | $-0.017$                                 |
| Cl       |       | In sphere 3 (Cl)            | $-0.006$                                 |
|          |       | Total spin magnetic moment in unit cell | 10.000 |
| DyOCl    | AFM   | In interstitial             | $-0.011$                                 |
| Dy1      |       | In sphere 1                | 4.967                                    |
| Dy2      |       | In sphere 2                | $-4.795$                                 |
| O3       |       | In sphere 3                | $-0.026$                                 |
| O4       |       | In sphere 4                | $-0.048$                                 |
| Cl5      |       | In sphere 5                | $-0.012$                                 |
| Cl6      |       | In sphere 6                | $-0.006$                                 |
|          |       | Total spin magnetic moment in unit cell | 0.147 |
| HoOCl    | FM    | In interstitial             | 0.049                                    |
| Ho       |       | In sphere 1                | 3.898                                    |
| O        |       | In sphere 2                | 0.076                                    |
| Cl       |       | In sphere 3                | 0.002                                    |
|          |       | Total spin magnetic moment in unit cell | 8.000 |
| HoOCl    | AFM   | In interstitial             | $-0.009$                                 |
| Ho1      |       | In sphere 1                | 3.970                                    |
| Ho2      |       | In sphere 2                | $-3.770$                                 |
| O3       |       | In sphere 3                | $-0.024$                                 |
| O4       |       | In sphere 4                | $-0.050$                                 |
| Cl5      |       | In sphere 5                | $-0.010$                                 |
| Cl6      |       | In sphere 6                | $-0.011$                                 |
|          |       | Total spin magnetic moment in unit cell | 0.200 |
ordering for the calculations of electronic and magnetic properties. The calculated spin magnetic moments for some cases are consistent with experimental data with maximum measured values of the order of 10.00 μ_B for both DyOCl and HoOCl compounds both in FM order. Our results with GGA + U + SOC scheme revealed that both DyOCl and HoOCl have insulating nature under FM ordering while they are metallic materials under AFM ordering. The magnetic nature of the compounds may render them suitable candidates for potential magnetic applications in the fields of biomedical and spintronic.

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