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Joël Martial Balkoulga, Antoine Béré, Sidiki Zongo, Viwanou Hounkpati, Moussa Sougoti, et al.. Structural and elastic properties of perovskite HoMnO<sub>3</sub> crystal structures from ab-initio calculations. Computational Materials Science, 2023, 229, pp.112402. 10.1016/j.commatsci.2023.112402 . hal-04178085

**HAL Id: hal-04178085**

**<https://hal.science/hal-04178085>**

Submitted on 29 Feb 2024

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# Structural and elastic properties of perovskite $\text{HoMnO}_3$ crystal structures from ab-initio calculations

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## Abstract

The structural and elastic properties of the oxide perovskite  $\text{HoMnO}_3$  have been investigated by density-functional theory (DFT) implemented on the Quantum ESPRESSO code for the hexagonal, orthorhombic, rhombohedral and cubic crystal structures in the non-magnetic (NM), ferromagnetic (FM) and antiferromagnetic (AFM) configurations. The results show that all these compounds are thermodynamically stable, the hexagonal and the orthorhombic being the most stables in agreement with experimental results. The calculated bulk modulus,  $B$ , is about  $168.5 \pm 1.0$  GPa and  $178.9 \pm 1.0$  GPa for hexagonal structure in FM and configurations, respectively, and  $188.7 \pm 0.6$  GPa and  $175.6 \pm 2.1$  GPa for orthorhombic structure in FM and AFM configurations, respectively. These values and those of the elastic constants  $C_{ij}$  in the present work are comparable to values recently obtained with DFT calculations and experimentally for other perovskites  $\text{RMnO}_3$  ( $R=\text{Eu, Gd, Tb and Dy}$ ). The calculated Poisson's ratio is about 0.19; 0.27; 0.23 and 0.3 for hexagonal, orthorhombic, rhombohedral and cubic structure, respectively. The calculated Pugh's ratio is about 1.30; 1.77-1.98; 1.54-1.60 and 2.11, respectively. These results show that the perovskite  $\text{HoMnO}_3$  tends to be brittle in hexagonal

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27 phase and ductile in cubic phase. In the orthorhombic or rhombohedral phase, it is near brittle-  
28 ductile boarder line.

29 **Keywords:** HoMnO<sub>3</sub>; manganite crystal structures; manganite elastic constants; ab initio  
30 calculations; Quantum Espresso

## 31 I. INTRODUCTION

32 The manganese-based perovskite oxides of the  $\text{RMnO}_3$  type recognized as multiferroic  
33 materials have attracted technological interest because they exhibit at least two ferroic orders,  
34 (anti)ferroelectricity, (anti)ferromagnetism and ferroelasticity, within a single phase offering  
35 the possibility of controlling the electrical polarization under a high magnetic field, or vice  
36 versa. They offer a wide range of potential applications such as high-density magnetic  
37 recording, magnetoresistive sensors and magnetic refrigeration [1], [2]. Under normal  
38 temperature and pressure conditions, the  $\text{RMnO}_3$  perovskites can be structurally divided into  
39 three subgroups depending on the size of the rare earth element R. The former subgroup with  
40 small rare earth ionic radius ( $R = \text{Sc, Y, Ho, Er, Tm, Yb and Lu}$ ), these perovskite crystallize  
41 in a hexagonal lattice named h- $\text{RMnO}_3$ , mainly in the  $P6_3cm$  space group. The second  
42 subgroup, with large rare earth ionic radius, crystallizes in an orthorhombic structure and is  
43 designated o- $\text{RMnO}_3$ , mainly in the  $Pnma$  space group. They are the compounds with  $R = \text{La,}$   
44  $\text{Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb and Dy}$ . The last subgroup ( $R = \text{Ho, Y or Dy}$ ), with medium  
45 rare earth ionic radius, crystallizes either in hexagonal or orthorhombic structure depending on  
46 the synthesis conditions. Experimentally, it has been reported that the hexagonal phase of  
47  $\text{RMnO}_3$  can be transformed into orthorhombic phase at high temperature and pressure [3], [4].

48 To our knowledge, there is no systematic study including different crystal systems (cubic,  
49 hexagonal, orthorhombic, rhombohedral, etc.) of such perovskite  $\text{RMnO}_3$  since some were  
50 synthesized under specific experimental conditions [5]. Indeed, previous theoretical works on  
51  $\text{HoMnO}_3$  reported the following crystal structures: hexagonal [6], [7]; orthorhombic [8], [9];  
52 rhombohedral [10], and none of these works dealt with different crystal systems.

53 In this work, we have carried out a systematic DFT study based on Quantum ESPRESSO  
54 calculations of the structural and elastic properties of perovskite  $\text{HoMnO}_3$  in its hexagonal (h-  
55 HMO), orthorhombic (o-HMO), rhombohedral (r-HMO) and cubic (c-HMO) structures. They

56 are in  $P6_3cm$ ,  $Pnma$ ,  $R\bar{3}c$  and  $Pm\bar{3}m$  space groups, respectively. It has to be noticed that  
57 there is a lack of experimental or theoretical data on elastic constants of this perovskite.  
58 Therefore, the objective of this study is to provide a better comparability of the obtained results.

## 59 **II. THEORETICAL APPROACHES**

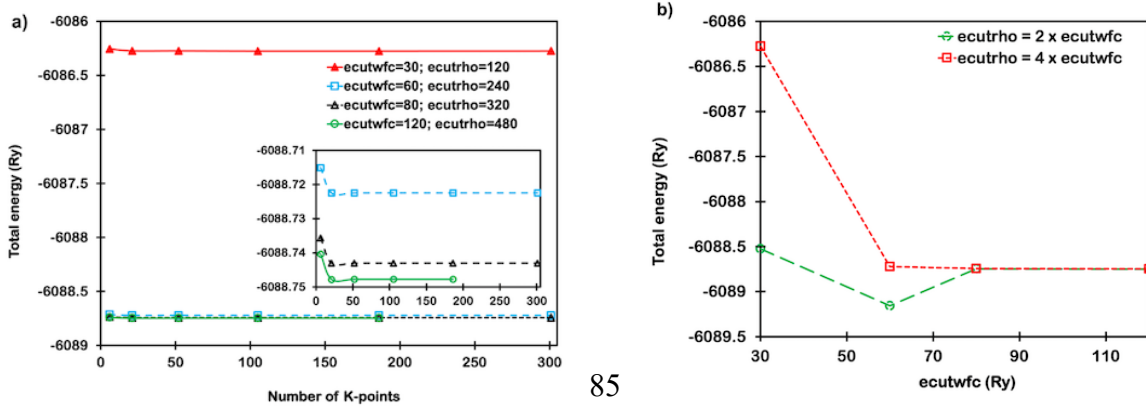
### 60 ***2.1. Potential and structural properties***

61 The Quantum Espresso code for first-principles calculations based on density functional  
62 theory (DFT) is employed as potential. This performs electronic structure calculations and  
63 materials (metals, insulators and semiconductors) modelling with high accuracy.

64 Quantum Espresso supports Norm-Conserving (NC), Ultrasoft (US), and Projector-  
65 Augmented Wave (PAW) pseudopotentials (PPs). It also supports exchange-correlation  
66 functions of the local density approximation (LDA), generalized gradient approximation  
67 (GGA), or more advanced type.

68 To run Quantum Espresso, some parameters are fixed. This includes, (i) the valence states  
69 describing the atomic cores; (ii) the pseudopotential describing the ion-electron interactions;  
70 (iii) the exchange-correlation functional; (iv) the convergence criterion on total energy for ionic  
71 minimization (etot\_conv\_thr); (v) the convergence criterion on forces for ionic minimization  
72 (forc\_conv\_thr); (vi) the k-point mesh to determine the first Brillouin zone; (vii) the kinetic  
73 energy cutoff for wavefunctions (ecutwfc) and (viii) the kinetic energy cutoff for charge density  
74 and potential (ecutrho). For this work, (i) the valence states are set to  $(5s^26s^{1.5}5p^66p^{0.5}d^1)$ ,  
75  $(3s^23p^63d^54s^2)$ , and  $(2s^22p^4)$  for the Ho, Mn, and O atoms, respectively; (ii) the ion-electron  
76 interactions are described by the PAW method [11]; (iii) the exchange-correlation functional  
77 employed is that of Perdew-Burke-Ernzerhof parameterization of the generalized gradient  
78 approximation (PBE-GGA) [12]; (iv) the energy convergence criterion for electronic self-  
79 consistency is set to  $10^{-6}$  u.a; (v) the atomic forces convergence criterion is set to  $10^{-4}$  u.a; (vi)

80 the k-point mesh is set to  $9 \times 9 \times 9$ ; (vii) the kinetic energy cutoff for wavefunctions is set to  
 81 80 Ry and (viii) the kinetic energy cutoff for charge density and potential is set to 400 Ry. It  
 82 has to be noticed that the values of these last three parameters are fixed after the energy  
 83 convergence test calculations (Fig 1).



84

85

86 *Fig1: Convergence test of total energy as a function of: a) k-points mesh; b) kinetic energy*  
 87 *cutoff for wavefunctions (ecutwfc). In (a), the convergence is assumed to occur with 52-points*  
 88 *that correspond to a 6 x 6 x 6 k-points grid and undependably of the ecutwfc value. In (b), the*  
 89 *convergence is assumed to occur with ecutwfc=80 Ry and undependably of the ecutrho value.*  
 90

91 Geometry optimizations are performed in the supercell method using the Broyden–Fletcher–  
 92 Goldfarb–Shanno (BFGS) quasi-newton algorithm [13]; all atoms were allowed to relax and  
 93 reach minimum energies when the atomic forces become less than  $10^{-4}$  u.a. as previously  
 94 mentioned.

95 When the lower energy relaxed structure is obtained, the formation energy is calculated to  
 96 ensure that the system is thermodynamically stable. For compound materials such as  $\text{HoMnO}_3$   
 97 in equilibrium with a reservoir of Ho, Mn and O atoms, the formation energy  $E_{form}(D)$  of a  
 98 given structure D is defined as [14]:

99 
$$E_{form}(D) = E_{total}(D) - \mu_{Ho} \times n_{Ho} - \mu_{Mn} \times n_{Mn} - \mu_O \times n_O \quad (1)$$

100 where  $E_{total}(D)$  is the total energy of the supercell while  $\mu_{Ho}$ ,  $\mu_{Mn}$  and  $\mu_O$  are the Ho, Mn and  
 101 O chemical potentials, respectively. The values of these chemical potentials have been obtained  
 102 from Quantum Espresso calculations in the C19\_alpha\_Sm prototype (space group = R-3m)  
 103 for holmium (Ho), Mn(cI58) prototype (space group = I-43m) for manganese (Mn) and BaP3  
 104 prototype (space group = C2/m) for oxygen (O). The quantities  $n_{Ho}$ ,  $n_{Mn}$ , and  $n_O$  correspond  
 105 to the numbers of Ho, Mn and O atoms, respectively. The numbers of atoms per unit cell and  
 106 its repartition per atomic specie,  $n_{tot}(n_{Ho}, n_{Mn}, n_O)$  are: 30(6, 6, 18) for h-HMO or r-HMO;  
 107 20(4, 4, 12) for o-HMO and 5(1, 1, 3) for c-HMO.

108 The most stable structure is obtained by comparing the energy of a given structure ( $i$ ) to a  
 109 reference structure (ref) by evaluating the relative energy  $\Delta E(i)$  defined as:

$$110 \quad \Delta E(i) = E_{form}(i) - E_{form}(ref) \quad (2)$$

111 where  $E_{form}(i)$  and  $E_{form}(ref)$  are the formation energies of the structure ( $i$ ) and the  
 112 reference structure, respectively. In present calculations, the reference structure is set to the h-  
 113 HMO structure in the FM configuration.

## 114 **2.2. Elastic constant calculations**

115 The elastic properties of a crystal can be characterized by independent elastic constants,  
 116 namely  $C_{ij}$ . The total number of independent components of the elastic constant tensor depends  
 117 on the symmetry of the crystal. There are two approaches for calculating elastic constants: the  
 118 energy-strain ( $E-\epsilon$ ) method and the stress-strain ( $\sigma-\epsilon$ ) method. For more details on these  
 119 methods, see the publications of [15], [16], [17]. From these two methods, the energy-strain is  
 120 a more common-place for calculations using DFT approach. In this method, the energy of the  
 121 crystal is calculated for different values of the strain  $\epsilon$ . Then, its evolution curve is fitted as a  
 122 function of  $\epsilon$  by a polynomial and the value of the second derivative at  $\epsilon = 0$  related to those of  
 123  $C_{ij}$  is deduced. It should be noted that there are two parameters to be chosen for this method:

124 the polynomial degree and the  $\varepsilon$  region on which the adjustment is performed. In the present  
 125 work, the study focuses on  $\varepsilon$  region ranging from -0.06 to 0.06 with a step of 0.02. This gives  
 126 rise to seven self-consistent energy calculations for a given  $C_{ij}$  calculation or their combination.  
 127 The fitting of polynomial of order 3 and 4 was performed, allowing the determination of  
 128 average values and deviations.

129 It is well known that the elastic computation via the energy–strain relationship can lead to  
 130 erroneous results at non-zero pressure. Then, when the elastic constants are calculated, the  
 131 elastic stabilities of the four investigated structures are tested according to the stability criteria  
 132 presented in Table 1.

133 *Table 1: Elastic stability of crystal systems*

Crystal systems	Point groups	Space groups	Born stability criteria [18]
<b>Cubic</b>	$m\bar{3}m$	$Pm\bar{3}m$	$C_{11} - C_{12} > 0; C_{11} + 2C_{12} > 0; C_{44} > 0$
<b>Hexagonal</b>	6mm	$P6_3cm$	$\begin{cases} C_{11} >  C_{12} ; 2C_{13}^2 < C_{33}(C_{11} + C_{12}) \\ C_{44} > 0; C_{66} > 0 \end{cases}$
<b>Orthorhombic</b>	Mmm	Pnma	$\begin{cases} C_{11} > 0; C_{11}C_{22} > C_{12}^2; \\ C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0 \\ C_{44} > 0; C_{55} > 0; C_{66} > 0 \end{cases}$
<b>Rhombohedral</b>	3m	$R\bar{3}c$	$\begin{cases} C_{11} >  C_{12} ; C_{44} > 0 \\ C_{13}^2 < \frac{1}{2}C_{33}(C_{11} + C_{12}) \\ C_{14}^2 < \frac{1}{2}C_{44}(C_{11} - C_{12}) = C_{44}C_{66} \end{cases}$

134

135 To predict the plastic behavior of materials, the most widely used criteria are the Poisson's  
 136 ratio,  $\nu = \frac{3B-2G}{2(3B+G)}$ , and the Pugh's ratio,  $\frac{B}{G}$ , where B is the bulk modulus and G is the shear  
 137 modulus. Each of these ratios is related to the competition between two mechanical processes,  
 138 fracture and plasticity. For a given material, if plasticity (fracture) is easier, then it will tend to  
 139 be ductile (brittle). The critical value is 0.26 and 1.75 for the Poisson's ratio and the Pugh's

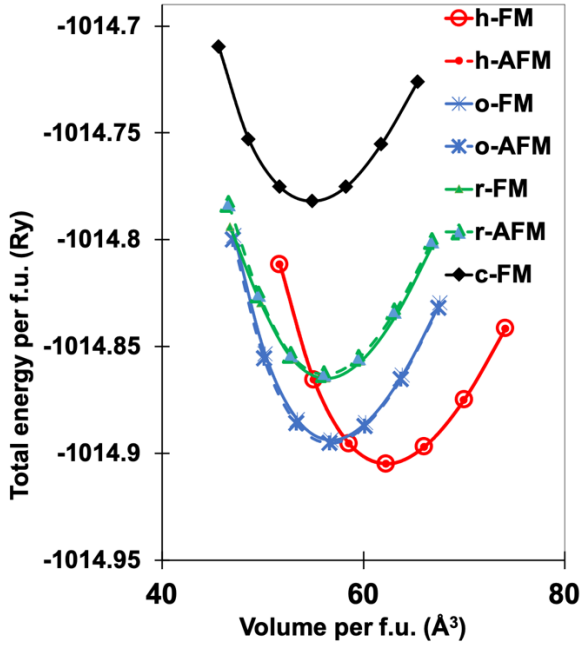


140 ratio, respectively [19][20]. The material is considered ductile (brittle) for a value of the  
141 Poisson's ratio or Pugh's ratio greater (smaller) than the corresponding critical value. In the  
142 present work, the Poisson's ratio and the Pugh's ratio are calculated according to Voigt-Reuss-  
143 Hill approximations [21].

## 144 **III RESULTS AND DISCUSSION**

### 145 *3.1 Structural and magnetic properties*

146 The structural properties which have been investigated are the lattice parameters, the  
147 formation energies and the relative stabilities of the different structures. The magnetic  
148 behaviour is determined by taking into account the non-magnetic (NM), ferromagnetic (FM)  
149 and the anti-ferromagnetic (AFM) spin configurations of the studied crystal systems (h-HMO,  
150 o-HMO, r-HMO and c-HMO). To this end, geometrical optimization calculations were first  
151 performed as described previously. The energy versus volume curves for different crystal  
152 phases in FM and AFM configurations of the  $\text{HoMnO}_3$  structure is presented in figure 2. It  
153 comes that the lowest energy configuration for  $\text{HoMnO}_3$  is the hexagonal structure (Ishibashi  
154 et al.). The least stable phase is the cubic structure. The minimum energy of the orthorhombic  
155 structure is closer to that of the hexagonal structure than the rhombohedral structure. The FM  
156 and AFM configurations of the hexagonal, orthorhombic or rhombohedral structure have  
157 almost identical evolution curves.



158

159 *Fig2: Energy versus volume for HoMnO<sub>3</sub> different crystal structures in FM and AFM*  
 160 *configurations. The number of atoms in the unit cell is 30, 20, 30 and 5 for h-HMO, o-HMO,*  
 161 *r-HMO and c-HMO, respectively. This gives rise to the unit formula (f.u.) per unit cell of 6, 4,*  
 162 *6 and 1 for h-HMO, o-HMO, r-HMO and c-HMO, respectively. On the legend, h-FM refers to*  
 163 *h-HMO in FM configuration.*

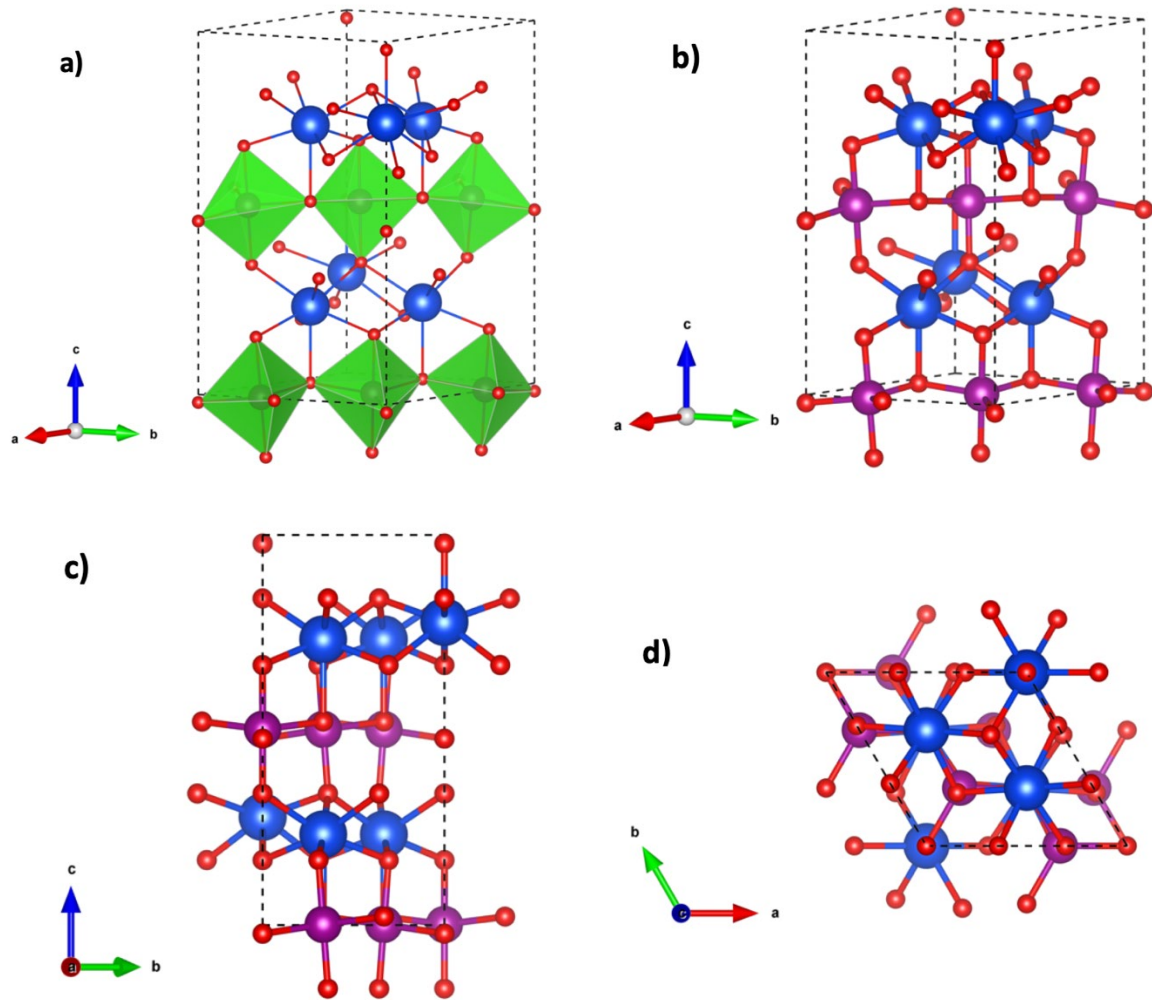
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### 165 3.1.1. Lattice parameters

166 The lattice parameters in the FM, AFM and NM configurations of h-HMO, o-HMO, r-HMO  
 167 and c-HMO relaxed atomic structures (figures 3-6) are presented in Table 2 in comparison with  
 168 reported theoretical and experimental data. The h-HMO lattice parameters values are in good  
 169 agreement with the recent experimental results of Ishibashi et al. [4]. Also, the o-HMO lattice  
 170 parameters are in agreement with the experimental results of Alonso et al. [22] than theoretical  
 171 results reported in [23], [8]. In the case of r-HMO and c-HMO lattice parameters, in absence  
 172 of experimental data, our results compare well with those of theoretical reported in [24].

173 The good agreement of the obtained values with those of experimental demonstrates the  
 174 accuracy of the quantum espresso calculations.

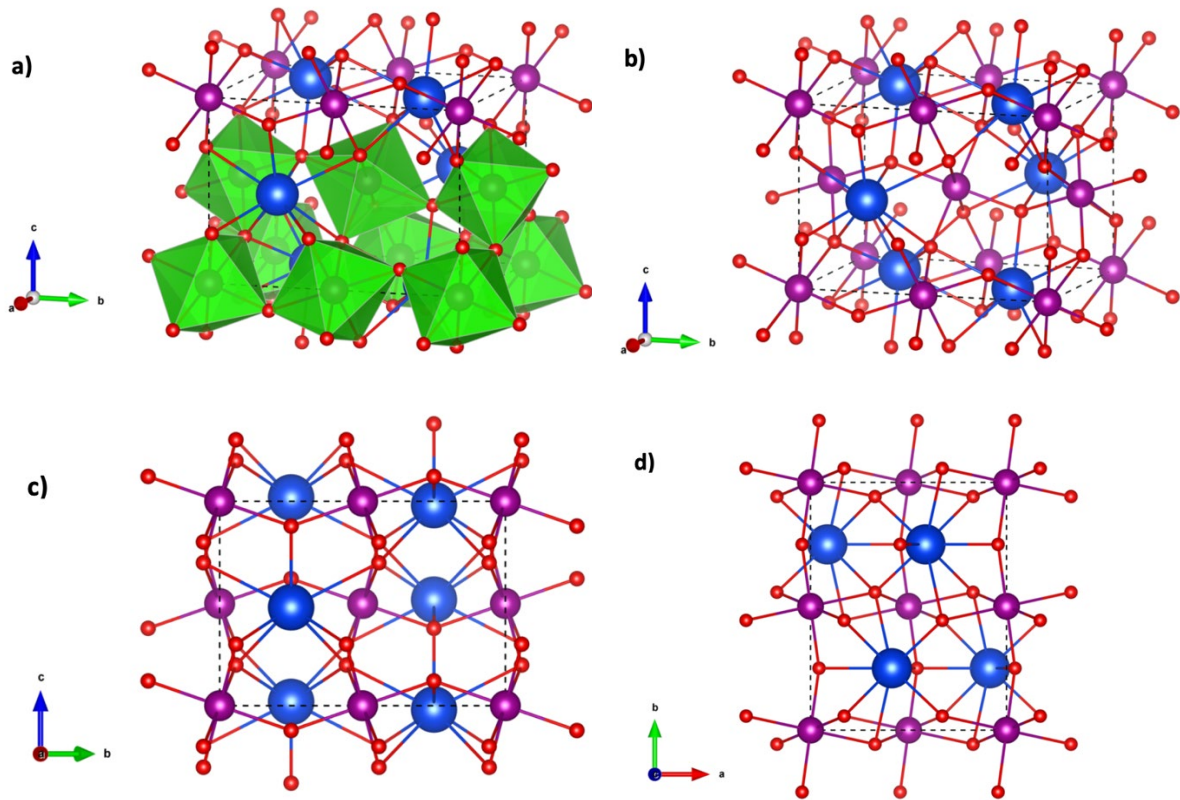
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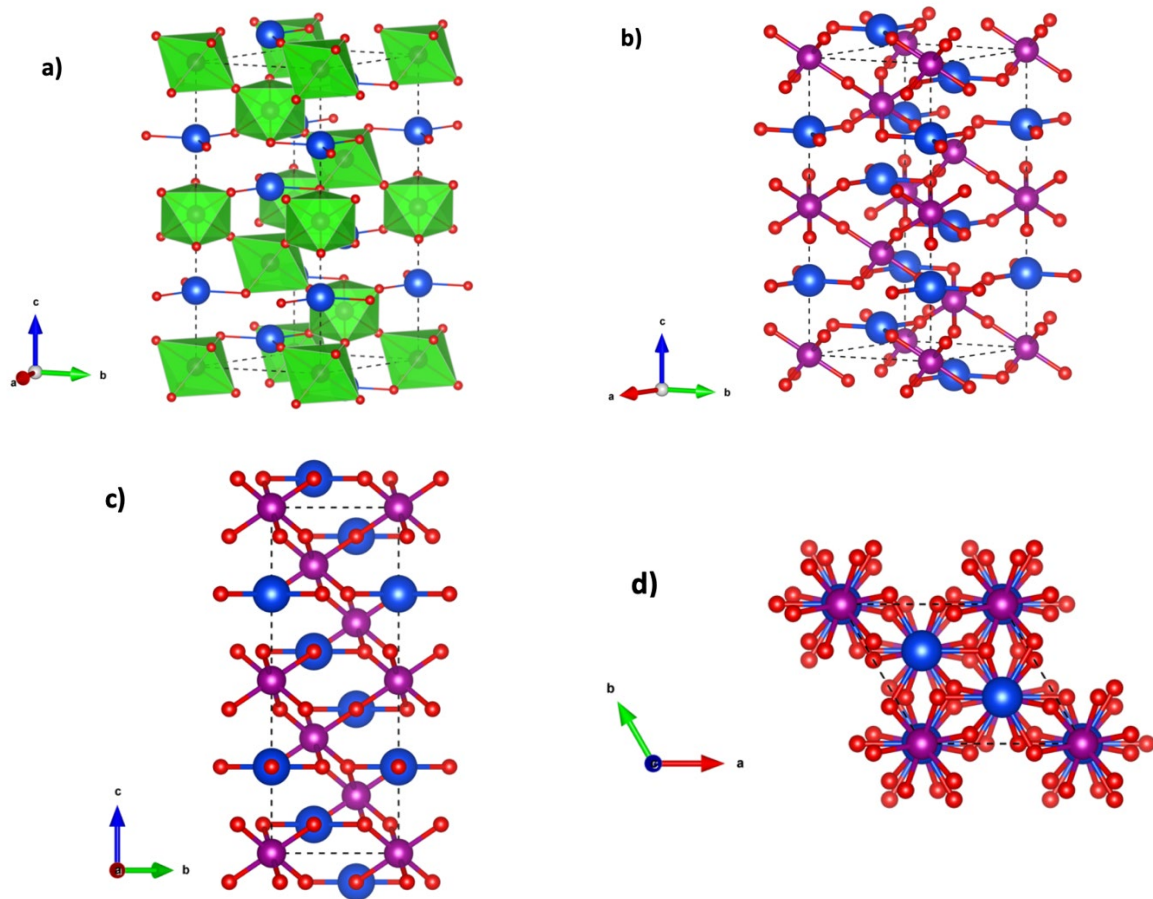
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177 *Fig3: Relaxed atomic structure of HoMnO<sub>3</sub> hexagonal crystal phase in FM configuration. a)*  
 178 *structure along [001]; (b) the real cell; (c) in a-direction; and in c-direction. The blue, purple*  
 179 *and red balls correspond to Ho, Mn and O atoms, respectively. The MnO<sub>5</sub> trigonal bipyramid*  
 180 *is represented in green. The unit cell is shown by dashed lines.*

181



182 *Fig4: Relaxed atomic structure of  $\text{HoMnO}_3$  orthorhombic crystal phase in FM configuration.*  
 183 *a) structure along  $[001]$ ; (b) the real cell; (c) in a-direction; and in c-direction. The blue, purple*  
 184 *and red balls correspond to Ho, Mn and O atoms, respectively. The  $\text{MnO}_6$  octahedra are*  
 185 *represented in green. The unit cell is shown by dashed lines.*



186

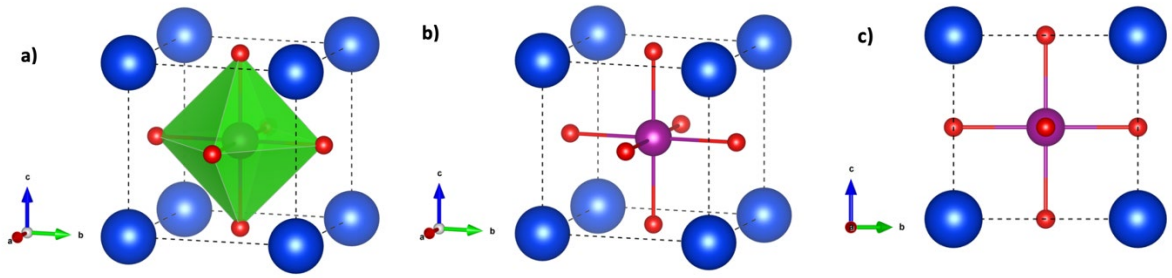
187 *Fig5: Relaxed atomic structure of  $\text{HoMnO}_3$  rhombohedral crystal phase in FM configuration.*

188 *a) structure along  $[001]$ ; (b) the real cell; (c) in a-direction; and in c-direction. The blue, purple*

189 *and red balls correspond to Ho, Mn and O atoms, respectively. The  $\text{MnO}_6$  octahedra are*

190 *represented in green. The unit cell is shown by dashed lines.*

191



192

193 *Fig6: Relaxed atomic structure of HoMnO<sub>3</sub> cubic crystal phase in FM configuration. a)*  
 194 *structure along [001]; (b) the real cell; (c) in a-direction; and in c-direction. The blue, purple*  
 195 *and red balls correspond to Ho, Mn and O atoms, respectively. The MnO<sub>6</sub> octahedra is*  
 196 *represented in green. The unit cell is shown by dashed lines.*

197

198 Table 2: Lattice parameters,  $a$ ,  $b$  and  $c$ , in angstrom ( $\text{\AA}$ ), equilibrium unit cell volume,  $V$ , in  
199  $\text{\AA}^3$ , formation energy,  $E_{form}$ , in electron-volt per atom (eV/atom), and relative energy,  $\Delta E$ , in  
200 millielectron-volt per atom (meV/atom) obtained with PBE-GGA-APW pseudopotentials DFT  
201 calculations for  $\text{HoMnO}_3$  crystal structures in non-magnetic (NM), ferromagnetic (FM) and  
202 antiferromagnetic (AFM) configurations.

Structure	$a$ ( $\text{\AA}$ )	$b$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )	$V$ ( $\text{\AA}^3$ )	$E_{form}$ (eV/atom)	$\Delta E$ (meV/atom)	Ref.
<b>h-HMO</b>							
NM	6.0562	6.0562	11.3160	359.68	-2.435	311	P.W. <sup>1</sup>
	NI <sup>2</sup>	NI	NI	NI	NI	394 <sup>3</sup>	[7]
FM	6.1463	6.1463	11.4181	373.51	-2.746	0	P.W.
	6.1300	6.1300	11.4340	372.06	-2.965	0	[24]
	6.1450	6.1450	11.4190	373.62	NI	NI	[4]
	6.1382	6.1382	11.4118	372.61	NI	NI	[25]
	6.1413	6.1314	11.4122	372.75	NI	NI	[26]
	6.1477	6.1477	11.4898	376.07	NI	0	[7]
AFM	6.1412	6.1412	11.4147	373.42	-2.746	0	P.W.
	6.1522	6.1522	11.5125	377.36	NI	-24 <sup>3</sup>	[7]
<b>o-HMO</b>							
NM	5.5440	7.3756	5.1065	208.81	-2.515	230	P.W.
	5.8461	7.3742	5.2681	227.11	-2.716	30	P.W.
FM	5.7100	7.4640	5.2570	224.06	-2.874	31	[24]
	5.8354	7.3606	5.2572	225.81			[22]
	5.7790	7.4410	5.2130	224.20			[23]
AFM	5.9039	7.3292	5.2387	226.68	-2.720	26	P.W.
	5.7500	7.2530	5.1800	216.01		679 <sup>4</sup>	[8]
<b>r-HMO</b>							
NM	5.3910	5.3910	12.4293	312.84	-2,450	296	P.W.
	NI	NI	NI	NI	NI	631	[10]
FM	5.4894	5.4894	12.9427	337.76	-2.637	109	P.W.
	5.4700	5.4700	12.8230	332.27	-2.874	122	[24]
	5.5960	5.5960	13.1210	355.84	NI	NI	[10]
AFM	5.4771	5.4771	12.9567	336.61	-2.632	114	P.W.
	NI	NI	NI	NI	NI	28; 112	[10]
<b>c-HMO</b>							
NM	3.7344	3.7344	3.7344	52.08	-2.240	506	P.W.
FM	3.8042	3.8042	3.8042	54.92	-2.411	334	P.W.
	3.8250	3.8250	3.8250	55.97	-2.639	357	[24]

<sup>1</sup> Present work

<sup>2</sup> Not indicated in the publication

<sup>3</sup> According to [7], the h-HMO relative energies with respect to the AFM configuration are 0.72 and 12.53 eV in FM and NM configurations, respectively. When taking the FM configuration as reference and considering that its supercell contains 30 atoms, we deduce that the h-HMO relative energies with respect to the FM configuration are -24 and 394 meV/atom in the AFM and NM configurations, respectively.

<sup>4</sup> According to [8], the o-HMO total energies are -112105.73656421 and -112104.738371 Ry in FM and AFM configurations, respectively. When considering that its supercell contains 20 atoms, we deduce that the o-HMO relative energy with respect to the FM configuration is 679 meV/atom in the AFM configuration.

203 Table 3 shows a comparison between the Mn-O and Ho-O interatomic distances. The  
 204 notation for Ho (Ho1 and Ho2), O (O1, O2, O3 and O4) and Mn is similar to those adopted in  
 205 Refs.[4]. As results, we obtain that the calculated interatomic distances in this present work are  
 206 in good agreement with reported experimental [4] and theoretical [8] works. In general, the  
 207 Ho-O interatomic distances are larger than the Mn-O distances, mainly the distances along of  
 208 the c-axis (Ho-O3 and Ho-O4). The results show small changes for interatomic distances and  
 209 tilting angles of the MnO<sub>5</sub> polyhedron in the FM and AFM configurations. Experimental  
 210 analysis of the chemical bonding is needed in order to explain these constataions.

211 *Table 3: Interatomic distance (Mn-O and Ho-O) and angles (O-Mn-O) of the MnO<sub>n</sub> polyhedron*  
 212 *for HoMnO<sub>3</sub> relaxed atomic structures in ferromagnetic (FM) and antiferromagnetic (AFM)*  
 213 *configurations.*

Structural parameter	Experimental [4]	Present work		Previously calculated [8]
		FM	AFM	
<b>Hexagonal phase</b>				
Ho1-O1/Å	2.308 x 3	2.312 x 3	2.312 x 3	
Ho1-O2/Å	2.324 x 3	2.270 x 3	2.270 x 3	
Ho1-O3/Å	2.380 x 1	2.292 x 1	2.292 x 3	
Ho2-O1/Å	2.244 x 3	2.308 x 3	2.308 x 3	
Ho2-O2/Å	2.359 x 3	2.263 x 3	2.263 x 3	
Ho2-O4/Å	2.410 x 1	2.405 x 1	2.405 x 1	
Mn-O1/Å	1.865 x 1	1.885 x 1	1.885 x 1	
Mn-O2/Å	1.960 x 1	1.890 x 1	1.889 x 1	
Mn-O3/Å	1.993 x 1	2.068 x 1	2.080 x 1	
Mn-O4/Å	2.092 x2	2.062 x 2	2.056 x 2	
01-Mn-O2/°		179.835	179.47	
03-Mn-O4/°		120.392	119.18	
<b>Orthorhombic phase</b>				
Ho-O/Å		2.225 x 1	2.226 x 1	2.313
		2.279 x 2	2.270 x 2	2.266
		2.292 x 1	2.293 x 1	
		2.501 x 2	2.509 x 2	
		2.586 x 2	2.560 x 2	
Mn-O/Å		1.922 x 4	1.904 x 2	1.898
			1.956 x 2	1.984
		2.228 x 2	2.269 x 2	
<b>Rhombohedral phase</b>				



Structural parameter	Experimental [4]	Present work		Previously calculated [8]
		FM	AFM	
Ho-O/Å		2.195 x 3	2.213 x 3	
Mn-O/Å		1.994 x 6	1.964 x 3	
			2.010 x 3	
<b>Cubic phase</b>				
Ho-O/Å		2.890 x 6		
Mn-O/Å		1.902 x 6		

214

### 215 3.1.2. Magnetic behavior

216 The formation energies  $E_{form}$  in the FM, AFM and NM configurations of h-HMO, o-HMO,  
 217 r-HMO and c-HMO crystal structures are presented in Table 2. The obtained values compare  
 218 well with those reported in [24]. The negative sign of the formation energies means that all  
 219 these crystal structures in different spin configurations are thermodynamically stable.

220 The magnetic behavior is discussed by evaluating the stability of corresponding  
 221 configuration compared with FM state. It appears from the relative energies  $\Delta E$  deduced from  
 222 formation energies (Table 2) that whatever the considered crystal structure, its magnetic  
 223 configuration (FM or AFM) is the most stable whereas its non-magnetic configuration (NM)  
 224 is the most unstable. Also, with respect to the orders of magnitude of the absolute values of the  
 225 relative energies, it appears unambiguous that the h-HMO structure is energetically more  
 226 favorable than the o-HMO, r-HMO and c-HMO structures. Our results also show that the FM  
 227 configuration is more energetically favorable than the AFM configuration for all crystal  
 228 structures, in agreement Hamioud et al. [8] for the case of o-HMO, using Wien2k code.  
 229 However, this is in opposite with the result reported by Chadli et al. [7] for the case of h-HMO  
 230 which calculations are done with the VASP code.

### 231 3.1. Elastic properties

232 The calculated elastic constants and bulk modulus are presented in Table 4. To our  
 233 knowledge, there is no experimental data on these parameters for HoMnO<sub>3</sub> crystal structures.

234 The existing results of the perovskite HoMnO<sub>3</sub> based on DFT calculations concern its bulk

235 modulus [7], [8], but not for the elastic constants  $C_{ij}$ . The present work is the first evaluation  
236 of the elastic constants of the perovskite  $\text{HoMnO}_3$  based on ab-initio calculations.  
237 Consequently, the calculated values could not be compared with experimental data. Also, the  
238 theoretical data on perovskite similar to  $\text{RMnO}_3$  type [23], [27], [28], [29] are given in Table 4  
239 to serve for comparison.

### 240 *3.1.1. Bulk modulus*

241 The h-HMO bulk modulus is  $168.5 \pm 1.0$  and  $178.9 \pm 1.0$  GPa for FM and AFM  
242 configurations, respectively. These values agree with those of 162.23 GPa and 169.34 GPa  
243 reported by Chadli et al. [7]. For the o-HMO structure, the calculated bulk modulus is  
244  $188.7 \pm 0.6$  GPa and  $175.6 \pm 2.1$  GPa for the FM and AFM configurations, respectively. These  
245 values are smaller than the value of 201.64 GPa reported by Hamioud et al. [8]. However, they  
246 are in agreement with experimental data reported by Muthu et al. [27] for others perovskites  
247  $\text{RMnO}_3$  that include  $\text{EuMnO}_3$  ( $185 \pm 6$  GPa),  $\text{GdMnO}_3$  ( $190 \pm 16$  GPa),  $\text{TbMnO}_3$  ( $188 \pm 9$  GPa)  
248 and  $\text{DyMnO}_3$  ( $192 \pm 8$  GPa) in orthorhombic phase. From these four perovskites, the  $\text{DyMnO}_3$   
249 is classified in the same subgroup as the  $\text{HoMnO}_3$ . The bulk modulus value of  $\text{HoMnO}_3$  is  
250 smaller than that of  $\text{DyMnO}_3$ . This result leads to the conclusion that  $\text{HoMnO}_3$  is more flexible  
251 than  $\text{DyMnO}_3$ .

### 252 *3.1.2. Elastic constants*

253 According to Tables 4 and 5, the elastic constants of the present work are 1.6 to 2.3 times  
254 higher than those given by Shell model calculations reported for the o-HMO structure [23] and  
255 for three other perovskites of  $\text{RMnO}_3$  type [28]. However, the calculated elastic constants are  
256 in the same order with those of DFT calculations and measured elastic constants as reported by  
257 Hemme et al. [29]. We conclude that a discrepancy is clear with results obtained from shell-  
258 model potential calculations.

259 Also, the calculated elastic constants satisfy the necessary and sufficient conditions for  
260 elastic stability given in Table 1 for each of the four investigated structures.

### 261 3.1.3. Mechanical behavior

262 Table 6 displays the calculated bulk modulus (B), shear modulus, (G) Young's modulus **E**,  
263 Poisson's ratio ( $\nu$ ) and Pugh's ratio (B/G) for HoMnO<sub>3</sub> different crystal structures in FM and  
264 AFM configurations according to Voigt-Reuss-Hill (VRH) approximations [21]. It is  
265 interesting to note that the bulk modulus values are comparable with those obtained from the  
266 strain-energy method (Table 4). For the FM (AFM) configuration, the deviation is about 1.06%  
267 (1.08%) for h-HMO, 0.21% (2.97%) for o-HMO, 0.85% (1.91%) for r-HMO and -0.73% for  
268 c-HMO.

269 The calculated values of  $\nu$  and B/G indicate that HoMnO<sub>3</sub> is brittle in the hexagonal phase  
270 ( $\nu=0.19$  and B/G=1.3) and ductile in the cubic phase ( $\nu=0.30$  and B/G=2.11). In the  
271 orthorhombic phase ( $\nu=0.26-0.28$  and B/G=1.77-1.98) or rhombohedral phase ( $\nu=0.23-0.24$   
272 and B/G=1.54-1.60), it is difficult to conclude with certainty whether the material is ductile or  
273 brittle. They are near brittle-ductile boarder line. According to [30], the calculated values of  $\nu$   
274 predict that HoMnO<sub>3</sub> tends to be ionic material ( $\nu\sim 0.1$ ) in the hexagonal phase, metallic  
275 material ( $\nu\sim 0.33$ ) in the cubic phase and covalent material ( $\nu\sim 0.25$ ) in the orthorhombic or  
276 rhombohedral phase.

277 The calculated value of Young's modulus of the hexagonal phase (E=305 GPa) is higher  
278 than that of  $219.2 \pm 10.6$  GPa reported experimentally [31].

279 The bulk modulus is an indicator of compound's resistance to the volume change. Usually,  
280 the bulk modulus increases when the cell volume decrease. Our calculated bulk moduli are  
281 about 154, 167, 172 and 181 GPa for the cubic, hexagonal, rhombohedral and orthorhombic  
282 phases, respectively. The cell volumes are 10.98, 12.45, 11.26 and  $11.36 \text{ \AA}^3/\text{atom}$ , respectively.

283 It appears that the above general trend doesn't correlate for the hexagonal phase which should  
284 be expected to have the greater value of bulk modulus in correlation with its cell volume. We  
285 conclude that an anomalous decreased as compared to the theoretical predictions is then  
286 observed.

287

Table 4 : Elastic constants ( $C_{ij}$ ) and bulk modulus ( $B$ ) in GPa obtained with PBE-GGA-APW pseudopotentials DFT calculations for  $\text{HoMnO}_3$  crystal structures in ferromagnetic (FM) and antiferromagnetic (AFM) configurations

Structure	Elastic constants							Bulk modulus	Ref.	
	$C_{11}$	$C_{22}$	$C_{33}$	$C_{12}$	$C_{13}$	$C_{23}$	$C_{44}$	$C_{66}$		$B$
<b>h-HMO</b>										
FM	293.4±1.3	293.4±1.3	385.3 ±5.6	69.1 ±0.4	103.0 ±4.7	103.0 ±4.7	175.5 ±0.2	83.3 ±0.3	168.5 ±1.0	P.W. <sup>5</sup>
AFM	293.1 ±1.3	293.1 ±1.3	384.7 ±5.9	69.3 ±4.1	103.0 ±7.4	103.0 ±7.4	175.8 ±0.2	83.4 ±0.4	168.4 ±1.0	P.W.
<b>o-HMO</b>										
FM	278.4 ±1.7	291.5 ±3.4	349.3 ±2.1	144.7 ±2.8	123.3 ±4.1	121.3 ±5.4	98.7 ±1.0	108.2 ±0.6	188.7 ±0.6	P.W.
	178	143	201				43			[23]
AFM	274.0 ±3.5	303.8 ±3.8	353.1 ±3.0	135.0 ±5.1	115.5 ±4.8	99.9 ±2.3	107.3 ±0.6	110.2 ±0.5	186.4 ±2.3	P.W.
<b>r-HMO</b>										
FM	364.6 ±0.7	364.6 ±0.7	221.1 ±2.5	146.2 ±4.1	93.9 ±3.3	93.9 ±3.3	148.5 ±1.8	80.5 ±0.9	173.9 ±14.5	P.W.
AFM	353.3 ±3.3	353.3 ±3.3	232.1 ±0.6	152.9 ±2.0	98.0 ±2.0	98.0 ±2.0	131.5 ±6.9	75.1 ±1.5	178.9 ±9.3	P.W.
<b>c-HMO</b>										
FM	305.5 ±8.4	305.5 ±8.4	305.5 ±8.4	79.5 ±9.2	79.5 ±9.2	79.5 ±9.2	54.7 ±2.3	54.7 ±2.3	153.7 ±3.7	P.W.

<sup>5</sup> Present work

Table 5 :Elastic constants in GPa of perovskite RMnO3 (R=Tb, Dy, Sm, Eu and Gd)

Structure	Elastic constants							Method	Ref.
	C <sub>11</sub>	C <sub>22</sub>	C <sub>33</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>23</sub>	C <sub>44</sub>		
o-TbMnO <sub>3</sub>	185; 209;	255; 277;	239; 257;	131; 147;	93; 117;	110; 128;	87; 91; 43;	DFT	[29]
	174; 249	268; 301	265; 275	141; 173	109; 118	121; 144	76		
		202±20	181±2			103±6	71±5	Expt. <sup>6</sup>	
	227	349	274	141	109	103	71	Expt.	
	170	150	197			48	Shell model	[23]	
o-DyMnO <sub>3</sub>	170	151	196			48		[23]	
o-SmMnO <sub>3</sub>	157	149	190			52			
o-EuMnO <sub>3</sub>	165	154	194			50	Shell model	[28]	
o-GdMnO <sub>3</sub>	166	143	198			45			

<sup>6</sup> Experimental

Table 6 : Calculated values of Bulk modulus ( $B$ ), shear modulus  $G$  (GPa), Young's modulus  $E$  (GPa), Poisson's ratio ( $\nu$ ) and Pugh's ratio ( $B/G$ ) for  $\text{HoMnO}_3$  different crystal structures in FM and AFM configurations according to Voigt-Reuss-Hill (VRH) approximations [21]

	$B_V$	$B_R$	$G_V$	$G_R$	$B_{VRH}$	$G_{VRH}$	$E$	$\nu$	$B/G$
<b>h-HMO</b>									
FM	169.14	164.27	133.33	122.29	166.71	127.81	305.39	0.19	1.30
AFM	169.06	164.21	133.37	122.29	166.63	127.83	305.40	0.19	1.30
<b>o-HMO</b>									
FM	188.64	187.97	96.45	93.97	188.31	95.21	244.43	0.28	1.98
AFM	181.30	180.76	103.66	100.99	181.03	102.33	258.31	0.26	1.77
<b>r-HMO</b>									
FM	179.81	165.06	116.59	107.83	172.43	112.21	276.63	0.23	1.54
AFM	181.83	169.92	106.93	100.78	175.88	103.86	260.33	0.25	1.69
<b>c-HMO</b>									
FM	154.83	154.83	78.02	68.92	154.83	73.47	190.31	0.30	2.11

## IV CONCLUSION

In summary, the structural and elastic properties of HoMnO<sub>3</sub> crystal systems have been investigated using accurate ab-initio calculations. The calculated formation energy shows that the rhombohedral or cubic structure should exist; however, the hexagonal and orthorhombic phases are energetically more favorable and the hexagonal crystal system is the most stable. The elastic properties have been for the first time, systematically studied. Due to the lack of experimental data, our results are predictive and are comparable to recent results on other perovskite RMnO<sub>3</sub> systems based on DFT calculations. The discrepancy is clear with results obtained from shell-model potential calculations. From this work, it may be concluded that such quantum espresso calculations are suitable and appropriate for the description of perovskite RMnO<sub>3</sub>, mainly the subgroup exhibiting hexagonal or orthorhombic crystal structure (R=Dy or Ho.)

**Acknowledgements:** The computations were performed at “CRIANN” (<http://www.crihan.fr>).



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