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In silico CrNF, a half-metallic ferromagnetic nitride-fluoride mimicking CrO₂.

Samir F. Matar^{a,*}

CNRS, ICMCB, Université de Bordeaux, 87 Avenue du Docteur Albert Schweitzer, 33600 Pessac, France
E-mail: matar@icmcb-bordeaux.cnrs.fr

* Correspondence and reprints: CNRS, Université de Bordeaux, ICMCB, 87 Avenue du Docteur Albert Schweitzer, 33600 Pessac, France, Tel.: +33-5-4000-2690; Fax: +33-5-4000-2761

E-mail address: matar@icmcb-bordeaux.cnrs.fr (S. F. Matar)

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Dedication:

This paper is dedicated to Dr Mario MAGLIONE, Director of the ICMCB-CNRS.

A B S T R A C T

Isoelectronic with CrO₂, CrNF is proposed in silico based on rutile derived structure with DFT computations. The ground state structure defined from cohesive energies is of MgUO₄-type, characterized by short covalent Cr-N and long ionic Cr-F distances. Like CrO₂ it is a half-metallic ferromagnet with $M = 2 \mu_B/FU$ integer magnetization with reduced band gap at minority spins. Major difference of magnetic response to pressure characterizes CrNF as a soft ferromagnet versus hard magnetic CrO₂. The chemical bonding properties point to prevailing covalent Cr-N versus ionic Cr-F bonding. Different synthesis route are examined.

1. Introduction

The search for synthetic novel materials with well targeted physical properties is a strategic route for proposing solutions in the field of Materials Science. Simple rules can be followed to devise new stoichiometries with specific properties. As an example boron nitride is an artificial binary which ‘mimics’ carbon: From the electronic count standpoint, the configurations of the neutral atoms: B ([He] $2s^2 2p^1$), N ([He] $2s^2 2p^3$) and C ([He] $2s^2 2p^2$), are such that “B + N = 2C”, *i.e.* summing up to 8 valence electrons on each side of the equality sign. Cubic boron nitride, *c*-BN is a good substitute for diamond with a hardness magnitude just below 10, which stands for the value assigned to diamond on the Moh scale of hardness *cf.* ref. [1] and therein cited works). Consequently beside structural characteristics, the way the same number of electrons is (re)distributed among chemically different atoms engaged in different interatomic bonds can be of relevance to predict new stoichiometries and properties. Considering an anionic substructure for a given tetravalent cation (A^{IV}), the isoelectronic relationship for valence shell states is established: $O + O \rightarrow N + F$, *i.e.* $2 \times (2s^2, 2p^4) \rightarrow (2s^2, 2p^3) + (2s^2, 2p^5)$. Nitride-fluorides of formulation $A^{IV}NF$ can be considered as pseudo-oxides, isoelectronic of $A^{IV}O_2$. Several nitride-fluorides exist, such as alkaline-earth Ba_2NF [2] and Mg_2NF [3] and transition metal based $TiNF$ [4] as well as $ZrNF$ [5]. Their investigations carried out within the well established quantum mechanical density functional theory DFT [6, 7] led to provide a better understanding of such mixed-anions compounds with potential properties like anisotropic electric conduction, optical anisotropy as well as its growth in thin films or at nanoscopic scales [8]. In $TiNF$ [9] and $ThNF$ [10] the arrangements of the N and F substructures were analyzed based on DFT computations focusing on the energetic parameters and the chemical bonding as well as the group-subgroup relationship.

CrO_2 , one of the rare ferromagnetic oxides at room temperature ($T_C \sim 400$ K) and $2 \mu_B$ magnetization per formula unit (FU) implicitly assigned to tetravalent Cr with $3d^2$ configuration, is known for its use in magnetic recording applications [11]. Since its early discovery [12], several works were devoted to its physical properties [13]. DFT band structure calculations go beyond the phenomenological description by identifying a half metallic ferromagnet HMF behavior [14,15], *i.e.* it is metallic for majority spins (\uparrow) and

insulating for minority spins (\downarrow) (cf. Fig. 5). The calculated magnetic band structure was confirmed later on by magneto-optic spectroscopy investigations [16].

The present work presents a proposition of the crystal, electronic, and magnetic structures as well as the bonding properties of chromium nitride fluoride CrNF, devised in the framework of the DFT from the electronic rules presented above and the group-subgroup relationships. Close relationships for the electronic and magnetic properties of CrNF are established with isoelectronic and structurally related CrO₂, well known in high density magnetic recording media during last century.

2 Computational details

Two computational methods within the DFT were used in a complementary manner. The Vienna *ab initio* simulation package (VASP) code [17,18] allows geometry optimization and total energy calculations. For this we use the projector augmented wave (PAW) method [18,19], built within the generalized gradient approximation (GGA) scheme following Perdew, Burke and Ernzerhof (PBE) [20]. The conjugate-gradient algorithm [21] is used in this computational scheme to relax the atoms. The tetrahedron method with Blöchl corrections [19] as well as Methfessel-Paxton [22] Brillouin-zone (BZ) integrals were approximated using the special k -point sampling of Monkhorst and Pack [23]. A large number of 150 k -points was used in the irreducible wedges of the respective BZ to perform total energy calculations. The optimization of the structural parameters was performed until the forces on the atoms were less than $0.02 \text{ eV}\text{\AA}^{-1}$ and all stress components less than $0.003 \text{ eV}\text{\AA}^{-3}$. Calculations assuming firstly a non spin polarized (NSP) configuration then spin polarized (SP) calculations were carried out.

Subsequent all-electron calculations, equally based on DFT with a GGA functional were carried out with the optimized parameters for a full description of the electronic and magnetic structures and the chemical bonding properties. They were performed using the augmented spherical wave (ASW) method [24,25] in a scalar relativistic implementation [26]. In the ASW method, the wave function is expanded in atom-centered augmented spherical waves, which are Hankel functions and numerical solutions of Schrödinger's equation, respectively, outside and inside the so-called augmentation spheres. In the minimal ASW basis set, we chose the outermost shells to represent the valence states and

the matrix elements were constructed using partial waves up to $l_{max} + 1 = 3$ for Cr and $l_{max} + 1 = 2$ for N and F. Low energy lying F(2s) were considered as core states. In order to optimize the basis set, additional augmented spherical waves are placed at carefully selected interstitial sites (IS). Self-consistency was achieved when charge transfers and energy changes between two successive cycles were such as: $\Delta Q < 10^{-8}$ and $\Delta E < 10^{-6}$ eV, respectively. The BZ integrations were performed using the linear tetrahedron method within the irreducible wedge [19]. The calculations are carried out assuming firstly spin degenerate, non spin-polarized (NSP), then spin polarized (SP) magnetic calculations for both ferromagnetic and antiferromagnetic long range orders are done for the identification of the ground state magnetic structure of the most stable model structure. The relative magnitude of the chemical bonding is obtained based on the overlap population analysis: S_{ij} , i and j being two chemical species. The crystal orbital overlap population (COOP) criterion is used [27]. In the plots positive, negative and zero COOP magnitudes indicate bonding, anti-bonding and non-bonding interactions respectively.

3 Geometry optimization and EOS.

3-1 Geometry optimization

The rutile ground state crystal structure of CrO₂ is tetragonal with $P4_2/mnm$ space group (SG) N° 136. For CrO₂ $a = 4.23$ Å and $c = 2.92$ Å with $d(\text{Cr-O}) \sim 1.87$ Å and two formula units (FU) per cell leading to the Cr₂O₄ stoichiometry. The atomic positions are Cr 2a at (0,0,0); O 4f at $(x,x,0; -x,-x,0; -x+1/2, x+1/2, 1/2; -x+1/2, -x+1/2, 1/2)$, $x \sim 0.305$ [6-10]. For CrNF, a starting setup model was done by ordering N and F at the O (4f) positions leading to the Cr₂N₂F₂ stoichiometry. By carrying out unconstrained geometry optimization runs, the symmetry becomes orthorhombic. Such symmetry is found in anion ordered rutile-type derivatives obeying group to subgroup relations examined by Baur [28] with two orthorhombic structures: CoReO₄ ($Cmmm$ SG N°65; $Z = 4$ FU) and MgUO₄ ($Imam$ SG N° 74; $Z = 8$ FU). Both exhibit cationic and anionic ordering (*cf.* Table 1) and constitute appropriate host structures for modeling the ternary compound CrNF. The two candidate structures are confronted through determining the ground state structure and deriving equilibrium values based on the energy-volume equation of state (EOS). Full analyses of the electronic and the magnetic structures as well as the properties of chemical bonding are subsequently done for the ground state structure properties.

For the purpose of geometry optimization and search for the ground state structure, non spin polarized (NSP) were carried out starting from CoReO_4 (based centered orthorhombic) and MgUO_4 (body centered orthorhombic) types [28]. The respective orthorhombic symmetries were preserved at self consistent convergence. The fully relaxed structure parameters and the corresponding energies and volumes are given in Table 1. The energies are close but point out to MgUO_4 –type as the ground state with $\Delta E = -0.175$ eV/FU. The distance trends of $d(\text{Cr-F}) > d(\text{Cr-N})$ shown in both sets of results follow from the ionic *versus* covalent bonding and interestingly $d(\text{Cr-O})$ is situated in-between: $d(\text{Cr-F}) \sim 1.93\text{-}2.00 \text{ \AA} > d(\text{Cr-O}) \sim 1.87 \text{ \AA} > d(\text{Cr-N}) \sim 1.85\text{-}1.77 \text{ \AA}$. The sequence of distances is found to follow inversely the sequence of electronegativity of the anions: $\chi_{\text{N}} (3.04) < \chi_{\text{O}} (3.44) < \chi_{\text{F}} (3.98)$. The resulting structures are shown in Fig. 1 highlighting the distorted CrN_3F_3 octahedra as it can be seen from the different Cr-N and Cr-F distances shown in Table 1, differentiated for Cr1 and Cr2 surroundings. It needs to be stressed that in both model structures the CrN_3F_3 motifs arrange along c direction into files of edge sharing octahedra, as in rutile.

The cohesive energies for CrNF candidate structures are obtained and compared with that of CrO_2 by subtracting the computed atomic energy of Cr ($E = -9.50$ eV) and the corresponding dimers from the total energy: $E(\text{O}_2): -11.21$ eV, $E(\text{N}_2): -20.78$ eV, $E(\text{F}_2): -3.71$ eV. Then $E_{\text{coh.}}(\text{CrNF } Cmmm) = -1.045$ eV/FU, $E_{\text{coh.}}(\text{CrNF } Imam) = -1.107$ eV/FU and $E_{\text{coh.}}(\text{CrO}_2: P4_2/mnm) = -1.303$ eV/FU. Clearly the oxide is more cohesive than the nitride fluoride which is more cohesive in its ground state $Imam$ MgUO_4 –derived structure. These results point out to the possibility of actually synthesizing the compound and presently investigated protocols are developed upon in the last section of the paper. Lastly testing of the disordering effects of N and F by partials occupations of their crystal lattice sites was done in MgUO_4 -type ground state structure, i.e. F(8i) and N(8h) led to a large raise of the energy by -1.08 eV/FU.

In view of the ferromagnetic ground state of CrO_2 with $2 \mu_{\text{B}}/\text{FU}$ magnetization, further geometry optimized calculations were carried out for isoelectronic CrNF considering two spin populations, i.e. spin polarized (SP) calculations. In both structural types a $2 \mu_{\text{B}}/\text{FU}$ was found at self consistent energy convergence with a larger volume and stabilized energy: $\Delta E(\text{CrNF } Cmmm) = -0.24$ eV/FU and $\Delta E(\text{CrNF } Imam) = -0.35$ eV/FU. This suggests a tetravalent character of Cr similarly to CrO_2 . This point is discussed further while deriving

the energy –volume equation of state (EOS) and the electronic and magnetic structures in next sections.

3.2- Energy-volume equations of states

For confronting the relative stabilities of two varieties in NSP and SP configurations, one needs establishing the energy-volume equation of state (EOS). In fact the calculated total energy pertains to the cohesive energy within the crystal because the solution of the Kohn-Sham DFT equations yields the energy with respect to infinitely separated electrons and nuclei. In as far as the zero of energy depends on the choice of the potentials, somehow it becomes arbitrary meaning it is shifted but not scaled. However the energy derivatives as well as the EOS remain unaltered. For this reason one needs to establish the EOS and extract the fit parameters for an assessment of the equilibrium values. This is done from (E, V) set of calculations around minima found from geometry optimization. The resulting $E = f(V)$ curves are shown in Fig. 2. They have a quadratic variation which can be fitted with 3rd order energy-volume Birch-Murnaghan EOS [29]:

$$E(V) = E_0(V_0) + [9/8]V_0B_0\left[\left(\frac{V_0}{V}\right)^{2/3}-1\right]^2 + [9/16]B_0(B'-4)V_0\left[\left(\frac{V_0}{V}\right)^{2/3}-1\right]^3,$$

where E_0 , V_0 , B_0 and B' are the equilibrium energy, the volume, the bulk modulus and its pressure derivative, respectively. The fit results in the inserts of Fig. 2 show the trend of smaller volumes and higher energies of the NSP forms versus SP pointing to stable magnetically polarized compounds. The energies are such that $\Delta E_{SP-NSP}(\text{CrNF } Cmmm) = -0.29$ eV/FU and $\Delta E_{SP-NSP}(\text{CrNF } Imam) = -0.35$ eV/FU. Interesting features appear for the zero pressure bulk modules which are systematically higher for the NSP configuration as with respect to SP as one would expect from the larger volume for the latter due to the magnetic (negative) pressure. At large volume the separation between the SP and NSP $E(V)$ curves is maximum while they meet at low volume. This is expected in as far as the effect of decreasing volume (increasing pressure) is to reduce the localization of the d states needed for the onset of the magnetic moment. Consequently the magnetization should vanish at high pressure, i.e. at volumes below the equilibrium.

3.3- Magnetic response to exerted pressure

From above an estimate of the pressure magnitude required to destroy the magnetization is obtained from the Birch relationship providing the pressure [29]:

$$P = (B_0/B') [(V_0/V')^{B'} - 1].$$

Taking the fit values B_0 , B' , V_0 of the SP curve for the MgUO_4 -derived structure and the volume V' as $V(\text{NSP})$, P is calculated to be 11 GPa. This value is much smaller than the one calculated for CrO_2 of 120 GPa [30]. CrNF is then assigned a “soft” magnetic behavior while CrO_2 is a “hard” ferromagnet. This is further illustrated with the plots of the volume change of the magnetization shown for MgUO_4 -type CrNF and for CrO_2 in Fig. 3. The magnetization increases with volume and reaches saturation with $8 \mu_B/4 \text{ FU}^{-1/2} \text{ cell}^{-1}$ for CrNF and $4 \mu_B/2 \text{ FU}^{-1} \text{ cell}^{-1}$ for CrO_2 . What needs highlighting in the plots are the different behaviors of the two compounds around the equilibrium volume V_0 indicated by a vertical line: in CrNF there is a nearly immediate decrease of the magnetization below V_0 whereas in CrO_2 the saturation magnetization is kept far below V_0 . This nicely reflects the pressure magnitudes above.

4 All-electrons calculations.

The electronic and magnetic structures and the chemical bonding properties were calculated for the ground state structure of CrNF with the optimized structure parameters. Calculations with the CoReO_4 -type CrNF led to similar results.

Firstly NSP calculations were done to assign a role of each chemical species in the valence band (VB) and conduction band (CB). With the ASW method one starts from neutral atoms; at self consistency (energy and charge) using 432 k -points generated from 1728 ($12 \times 12 \times 12$) k -points in the orthorhombic BZ, there is charge redistribution between the atomic species. This does not translate the ionic picture as F^- despite the large ionic character of fluorine but the charge transfer is actually observed from Cr to N, F and IS, in agreement with the expectations of chemistry, i.e. from the metallic species to the anions (N, F) and IS which receive charge residues, i.e. less than 0.1 electron.

4.1 Non magnetic calculations and bonding properties.

The NSP site projected DOS (PDOS) accounting for site multiplicity are shown in Fig. 4. The energy reference along x is at the Fermi level E_F crossing a large PDOS intensity

arising from Cr d states which are mainly centered in the empty conduction band, above E_F . For the sake of clarity we do not show small contribution PDOS arising from IS. The lower part of the valence band (VB) is dominated by N(2s) at ~ -14 eV then F(2p) in the range $\{-10, -7$ eV $\}$ and N(2p) in the range $\{-5, -1$ eV $\}$. The PDOS below the two p blocks point to a larger Cr-N mixing than Cr-F. This is further made explicit in the analysis of the chemical bond in next section. Besides the mixing of states the NSP DOS allow assessing the instability of the compound from the large Cr PDOS at E_F in such a non magnetic configuration. The mean field Stoner theory of band ferromagnetism [31] can be applied to address the tendency for spin polarization. The total energy of the spin system results from the exchange and kinetic energies. Referring the total energy to the non-magnetic state, this is expressed as: $E = constant\{1 - \mathcal{J}n(E_F)\}$. In this expression, \mathcal{J} (eV) is the Stoner integral, which is calculated and tabulated for the metals by Janak [32] and $n(E_F)$ (1/eV) is the PDOS value for a given state -mainly d - at the Fermi level in the non-magnetic state. If the unit-less Stoner product $\mathcal{J}n(E_F)$ is larger than 1, E is lowered and the system stabilizes in a magnetically ordered configuration. Then the product $\mathcal{J}n(E_F)$ provides a criterion for the stability of the spin system. From ref. [32] the value of $\mathcal{J}\{\text{Cr}(3d)\}$ is 0.38 eV. With $n(E_F)$ value of 9 eV^{-1} , the calculated $\mathcal{J}n(E_F)$ is 3.4 and the Stoner criterion $1 - \mathcal{J}n(E_F)$ is largely negative leading to energy lowering upon the onset of magnetization, *i.e.* intra-band spin-polarization should occur when spin polarization is allowed. Subsequent spin polarized (SP) calculations with equal initial \uparrow and \downarrow spin populations, were carried out. At self-consistency a finite magnetization can be identified within an implicit long range ferromagnetic order. Nevertheless if magnetic exchange energy is not sufficient, zero local moments can result, so that the calculations are not biased initially. This also depends on of the BZ mesh precision, *i.e.* the calculations are usually carried out in steps of increasing precision until no more changes are observed in the variational energy and the magnetic moments.

The lower panel of Fig. 4 shows the bonding characteristics based on the analysis of the overlap populations S_{ij} with the COOP criterion. The bonding within the valence band VB is mainly between chromium on one hand and N and F on the other hand. It is differentiated between the two chromium sites with Cr1-F at -10 eV, Cr2-N at -4 eV. Note the low magnitude Cr2-F COOP versus Cr1-N. The overall prevalence of Cr-N over Cr-F follows the shorter Cr-N versus Cr-F distances and signals the rather covalent nature of the nitride fluoride. The itinerant Cr- d states mix with the p -states of N and F following their PDOS

positions in the DOS panel. The bonding between the two anionic sublattices is of antibonding nature because of the involvement of their states in the bonding with Cr. The large antibonding Cr1-F E_F COOP's are due to the near saturation of F-2p i.e. close to $2p^6$ so that the electrons brought by the Cr-F bond go into anti-bonding COOP's. This is opposed to the Cr-N COOP's at E_F which have much less intensity. The large anti-bonding COOP's at E_F is another signature of the instability of the nitride fluoride in such a spin degenerate configuration.

4.2 Ferromagnetic state and search for the magnetic ground state.

Upon charge and energy self-consistent convergence the total variational energy decreases largely with respect to the NSP configuration by $\Delta E(\text{SP} - \text{NSP}) = -1.41$ eV/cell. This gain of energy is due to the magnetic exchange leading to the onset of a magnetic moment as it is shown below. The total magnetization is $8.0 \mu_B/4$ FU, i.e. $2.0 \mu_B/\text{FU}$ with different local spin moments distributions: $M(\text{Cr1}) = 2.183 \mu_B$, $M(\text{Cr2}) = 2.317 \mu_B$; $M(\text{F}) = 0.025 \mu_B$ and $M(\text{N}) = -0.348 \mu_B$ with the remaining contributions from IS (interstitial part). The negative moment on nitrogen is of induced nature and arises from the Cr-N strong hybridizing shown in the preceding section. This result indicates anew, i.e. with respect to section 3 results, the formal tetravalent Cr^{IV} oxidation state ($3d^2$).

In fact the integer total magnetization results from the contribution of all the chemical constituents, not only Cr. It is illustrated in the plot of the SP PDOS shown in Fig. 5. The magnetic exchange causes the majority spins to shift down in energy and the minority spins to shift up in energy, proportionally to the magnitude of the developed magnetic moment. This is actually observed for Cr d states and less for F whereas the opposite is observed for s and p states of nitrogen which possesses a negative moment. The striking feature is observed at the Fermi level with large PDOS for \uparrow spin mainly due to Cr1 and Cr2 and a gap opening of ~ 0.5 eV for \downarrow spin. Comparing the SP DOS with those formerly obtained for CrO_2 in lower panel of Fig. 5 (ref. [15]) -low energy lying O(2s) are not shown-, similarities can be traced out as to the metallic \uparrow spin and the gap opening at \downarrow spin. However the gap magnitude of ~ 2 eV is much larger than the band gap in CrNF. This arises from the larger covalent overall Cr-N bonding versus Cr-O. It also contributes to explain the different magnetic responses of the two compounds to pressure as discussed above.

Lastly for a search of the magnetic ground state, antiferromagnetic AF orders were enforced. This can be justified in so far that CrN is AF in its orthorhombic structure (cf. [33] and therein cites references).

The $\text{Cr}_1\text{Cr}_2\text{N}_2\text{F}_2$ stoichiometry in the MgUO_4 -type ground state structure (Table 1) allows splitting the unit cell into two magnetic subcells with one $\text{Cr}_1\text{Cr}_2\text{N}_2\text{F}_2$ subcell as (UP SPINS) and the other $\text{Cr}_1\text{Cr}_2\text{N}_2\text{F}_2$ subcell as (DOWN SPINS), thus enforcing an AF of *G*-type, i.e. with antiparallel alignment of the atoms within a plane. At self consistent energy convergence there is full compensation of spins and an energy difference $\Delta E(\text{SP-F} - \text{SP-AF}) = -0.13 \text{ eV/FU}$, thus favouring the SP-Ferro state.

A-type AF order between planes was simulated by a double supercell along *c*. The calculations also favoured the SP-F state with $\Delta E(\text{SP-F} - \text{SP-AF}) = -0.17 \text{ eV/FU}$. Then the long range order of CrNF ground state is ferromagnetic.

5 Conclusions and synthesis routes prospects

Isoelectronic rules and (space)group-subgroup relationships coupled with quantum mechanical computations of energy derived quantities within DFT have been shown in earlier works to allow prediction of new materials as 2D and 3D carbon related boron-nitrogen binaries and carbon-boron-nitrogen ternaries. These rules applied here to the anionic sublattice in the prominent material CrO_2 and replacing oxygen by nitrogen and fluorine providing CrNF, lead to results that let expect an interesting material with new properties especially magnetic ones having close relationship with the oxide. It is expected that such rules can be generalized to propose to the experimentalists other new materials in the future. In view of the favorable cohesive energies of CrNF in both rutile derivative model structures and the identified close relationship with technologically important CrO_2 , synthetic routes are presently being evaluated mainly along different protocols:

- a- the ammonolysis of chromium fluoride precursor such as the protocol used on ZrF_4 for obtaining ZrNF [34];
- b- the method using fluorinated fluxes on CrN following a protocol proposed [5] for preparing ZrNF.

The latter protocol seems relevant from the electronic structure characteristics of CrNF, whereby within CrN, covalent Cr-N bonding is expected to be modified but still keep prevalent upon introducing fluorine either by F_2 fluxes or by use of F_2 pressure [35].

Other aspects related to the temperature and other preparation conditions (bulk, films...) are also under consideration.

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Figures

Fig.1 (color): CrNF in CoReO₄ (top) and MgUO₄ (bottom) ordered rutile derivatives highlighting the edge sharing mixed anion (N,F) octahedra at Cr1 (grey) and Cr2 (yellow) sites.

Fig.2 Energy-volume curves for CrNF in CoReO₄-type for 2 FU (top) and MgUO₄-type for 4 FU (bottom) in spin degenerate (NSP) and spin-polarized (SP) configurations and fit parameters from Birch-Murnaghan equations of states.

Fig.3 Plots of the total magnetization versus volume change in CrNF in MgUO₄-type calculated ground state structure for 4 FU (top) and in CrO₂ for 2 FU (bottom). Connecting lines are shown as a guide for the eye.

Fig.4 (color) CrNF with ground state MgUO₄ structure: Spin degenerate site projected DOS (top) and chemical bonding (COOP).

Fig. 5 (color) Site and spin projected density of states of CrNF in ferromagnetic ground state (top) and CrO₂ (bottom). Gap is indicated by large arrow.

TABLE

Table 1: Optimized structural parameters for CrNF in CoReO₄ and MgUO₄ models.

Structure	Unit Cell		Positional parameters		
	$a, b, c / \text{\AA}$		x	y	z
CrNF <i>CoReO₄-type</i>	6.133	Cr1(2a)	0	0	0
<i>Cmmm</i>	6.647	Cr2(2c)	0.500	0	0.500
$Z = 2 \text{ FU}$	2.671	F(4i)	0	0.290	0
		N(4h)	0.209	0	0.500
Short distances / \AA					
d(Cr1-F)	1.93				
d(Cr1-N)	1.78				
d(Cr2-F)	1.93				
d(Cr2-N)	1.85				
Energy / eV/2FU	-44.23				
<hr/>					
	$a, b, c / \text{\AA}$		x	y	z
CrNF <i>MgUO₄-type</i>	6.860	Cr1(4e)	0	0.028	0.250
<i>Imam</i>	6.200	Cr2(4b)	0	0.500	0
$Z = 4 \text{ FU}$	5.474	F (8i)	0.290	0.022	0.250
		N (8h)	0	0.208	0.001
Short distances / \AA					
d(Cr1-F)	1.98				
d(Cr1-N)	1.81				
d(Cr2-F)	2.00				
d(Cr2-N)	1.77				
Energy / eV/2FU	-44.58				

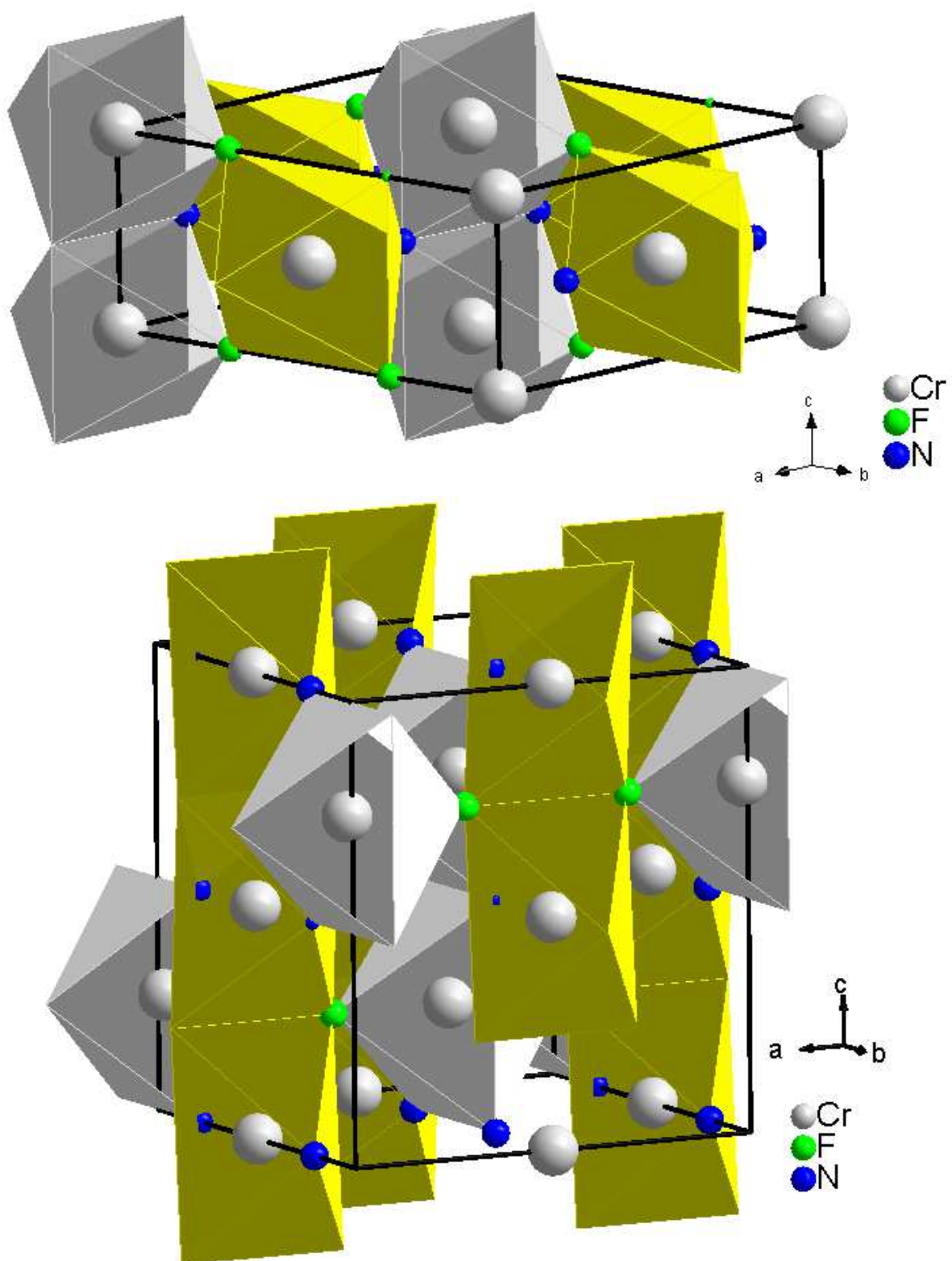


FIG. 1

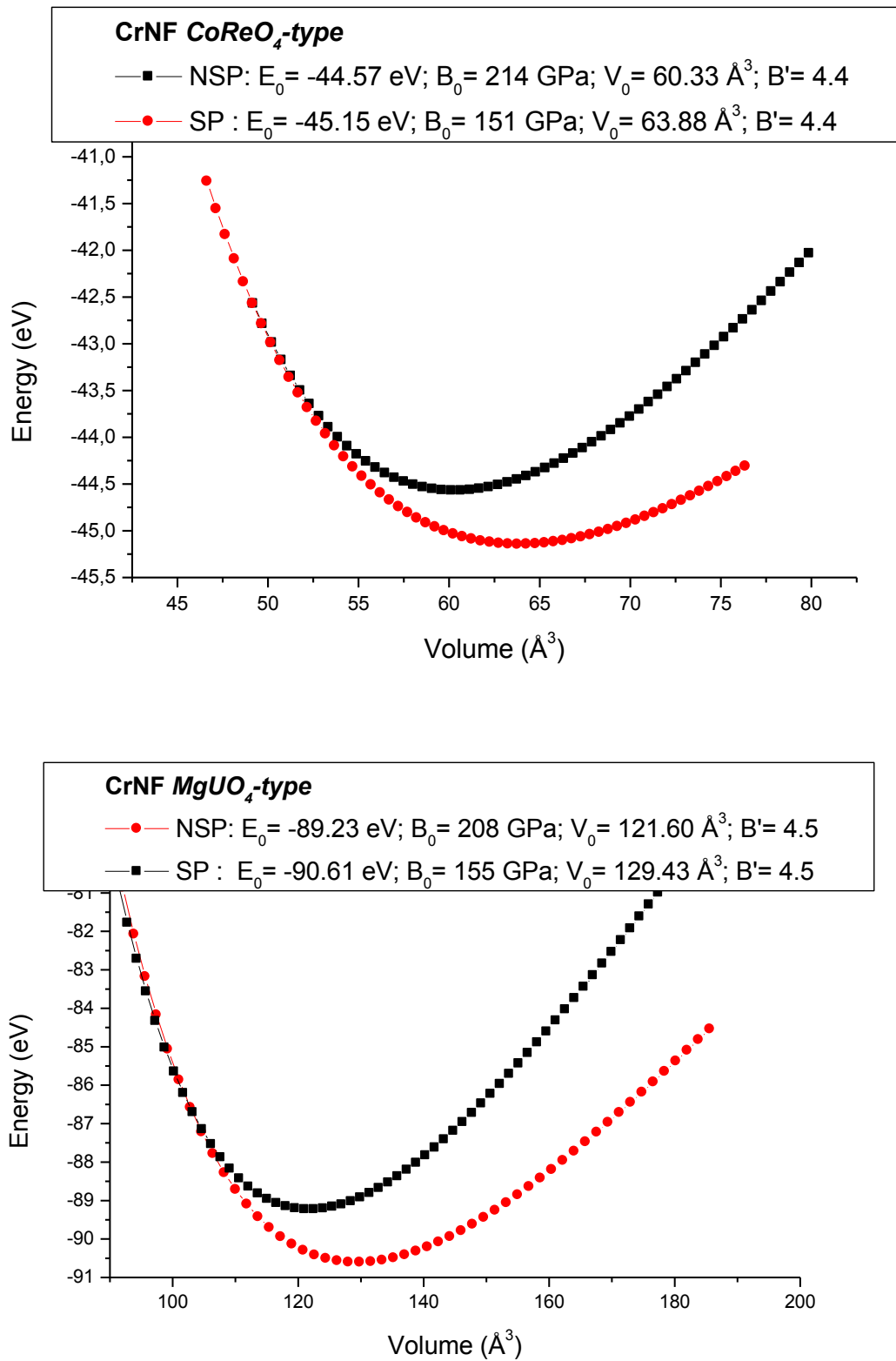


FIG. 2

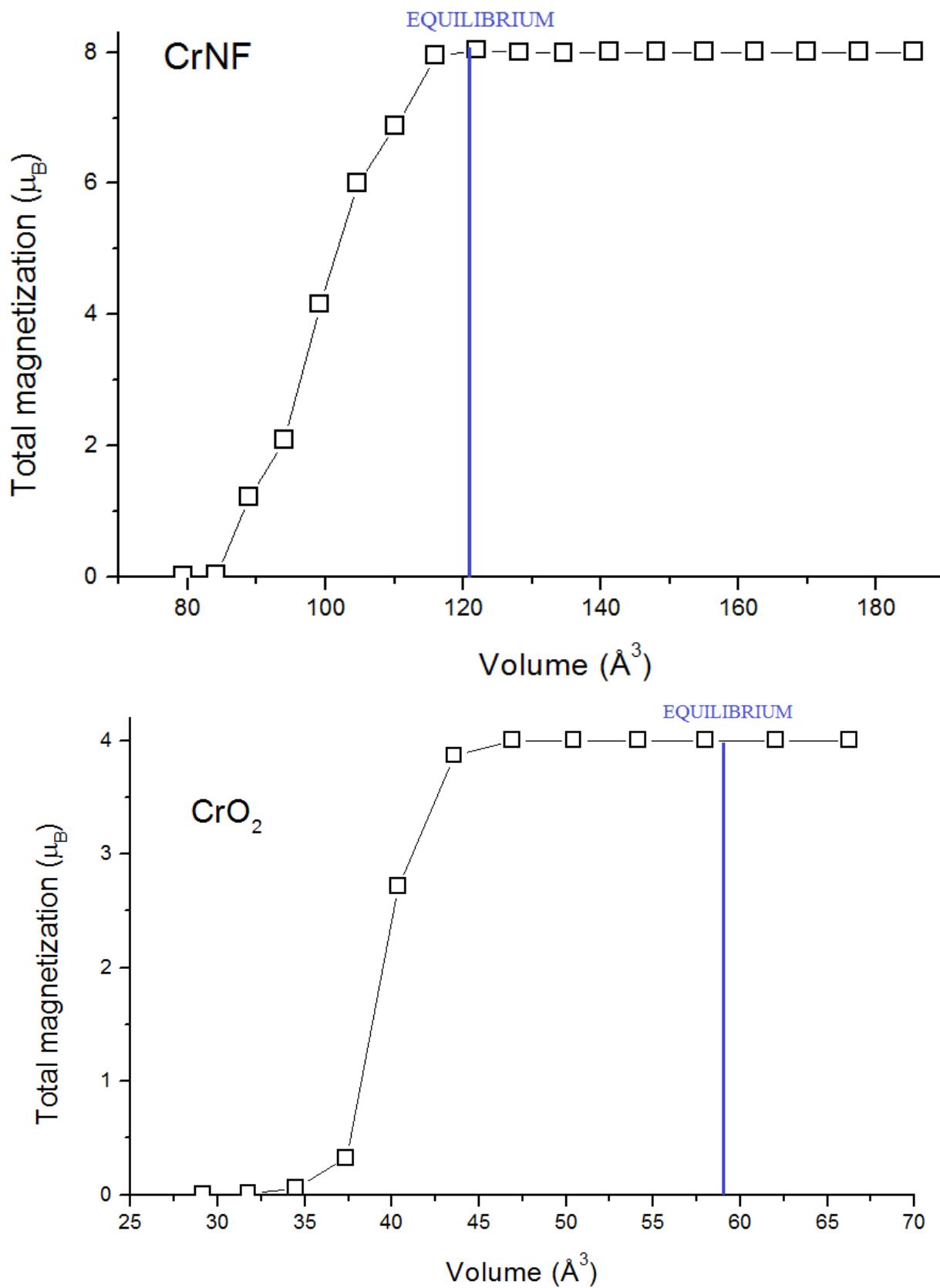


FIG. 3

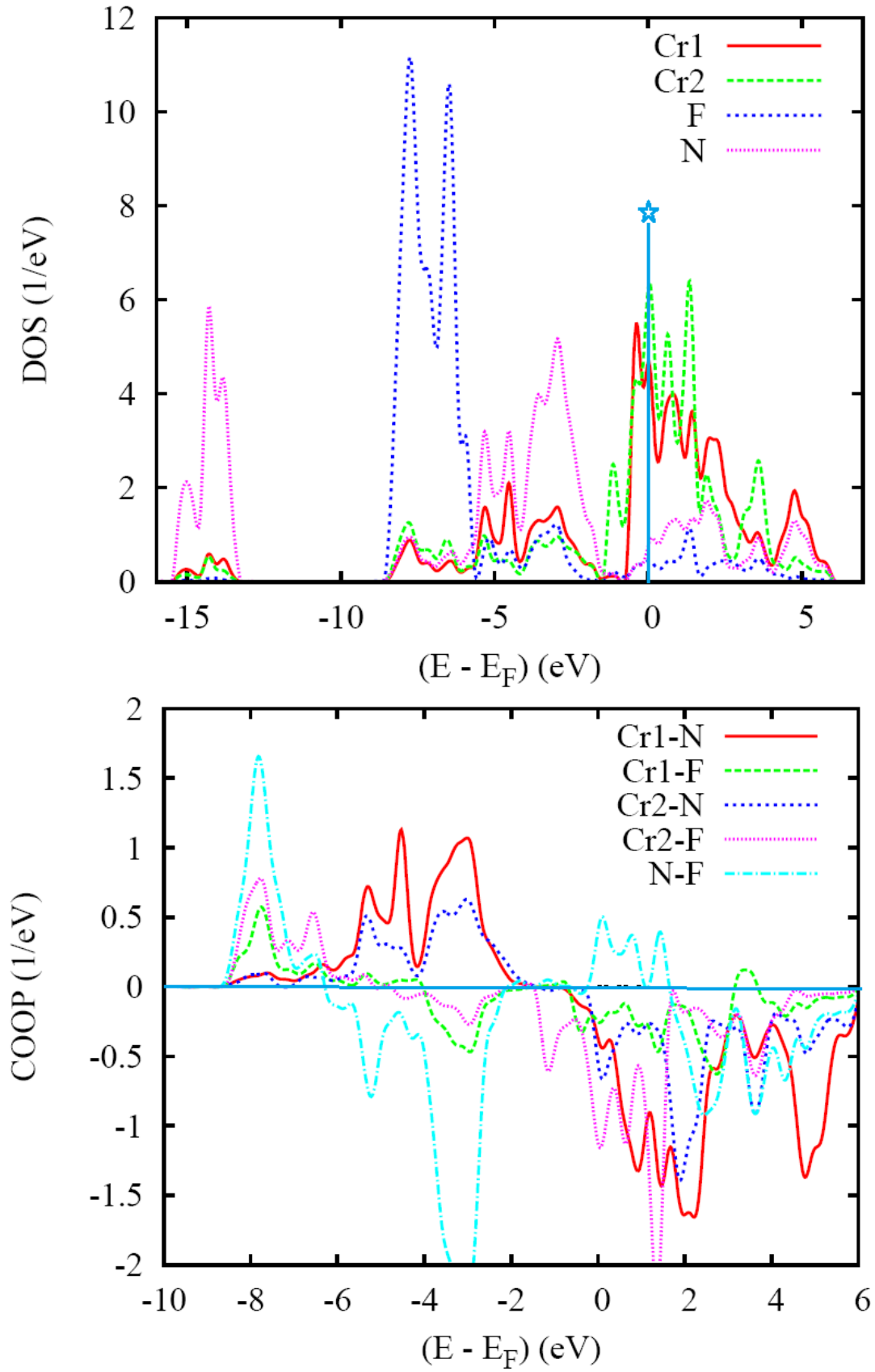


FIG.4

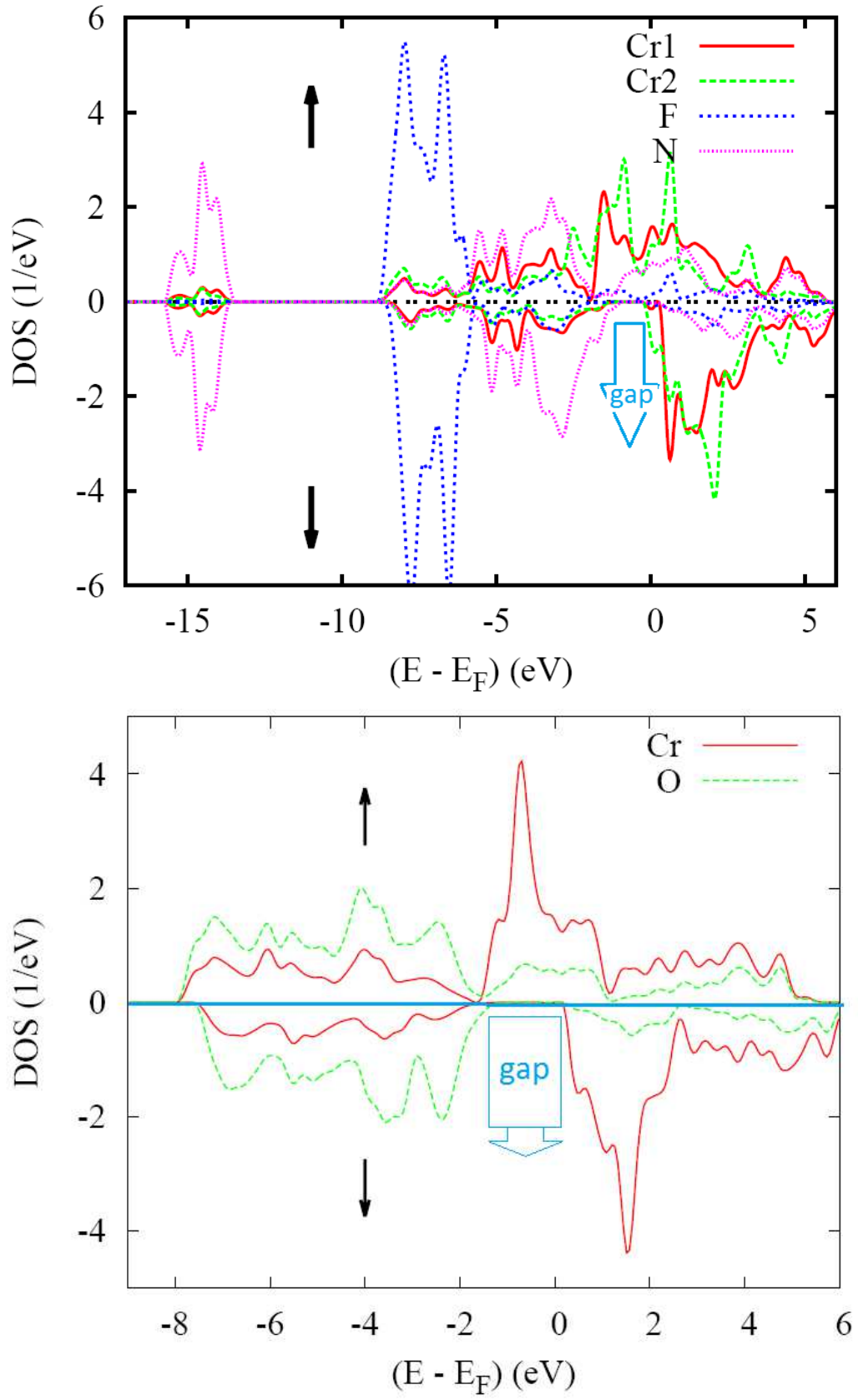


FIG. 5