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First principles investigation of the crystal and electronic structures of CeNCl and “CeNF”

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Abstract:

Based on DFT energy discrimination and detailed electronic and bonding properties, it is shown that the hitherto unexplored cerium nitride fluoride can be obtained in rhombohedral ThNF structure whereas actual CeNCl is confirmed in the early determination PbFCl-like structure. The respectively adopted 3D and 2D like structures are assigned to the major role played by the F polarizability, four times smaller than Cl. In their ground state both compound are found small gap insulators with 1.9 eV (CeNCl), 1.8 eV (CeNF) compared to insulating isoelectronic cerine CeO₂ with 2.2 eV band gap. The bonding shows balance between covalence brought by Ce–N bond versus ionic Ce–F(Cl) bonding and $d(\text{Ce–N}) < d(\text{Ce–F(Cl)})$ distances. Synthesis routes for CeNF are proposed.

Keywords: Mixed-anions, crystal structure, iono-covalent, DFT, COOP.

1. Introduction

The search of mixed anions compounds is an active field of research in so far that they offer original structural, physical and chemical properties related with the iono-covalent bonds. Such compositions refer on one hand to single anions mixtures as in layered PbFCl-type structure of BiOF, known for its use in ionic conductor solid electrolytes [1] as well as in more complex recently identified $Ba_{18}F_{18}In_8S_{21}$ and $Ba_9F_{10}In_4S_{10}$ low dimensional sulfide-fluorides [2] and on the other hand to poly-anionic constituents as phosphate anion associated to molybdate and tungstate anions in $Rb_2Bi(PO_4)(MO_4)$, $M = Mo, W$ [3]. In this context nitride-halides of formulation $A^{IV}NX$ (X : halogen) can be considered as pseudo-oxides being isoelectronic with $A^{IV}O_2$. A^{IV} stands for a tetravalent element such as a transition metal in $Ti^{IV}NF$ [4] and $Zr^{IV}NF$ [5]. Most of nitride-halides are single member, mainly with $X = F$. However in the case of Th^{IV} the whole $ThNX$ series exists, i.e. for $X = F, Cl, Br, I$ [6]. Interestingly, $ThNF$ is rhombohedral while the other $ThNX$ are tetragonal with a PbFCl-like structure. This structure is also adopted by $CeNCl$ which is the only rare earth nitride halide [7]. Recent review on layered nitride halides MNX ($M = IVB$ transition element and $X = Cl, Br, I$) with orthorhombic $FeOCl$ -type structure point out to superconducting properties evidenced upon partial intercalation with alkali elements [8].

Electronic structure, phase stability from energy criteria and chemical bonding properties are nowadays accessible with quantum theoretical density functional theory DFT [9,10] based methods. In recent years such methodology was used to investigate the physical properties including magnetic ones of nitride fluorides [11-14]. For instance $CrNF$ [14] was found to mimic the well known rare room temperature ferromagnetic oxide: CrO_2 used in high density magnetic recording, with major difference of magnetic response to pressure characterizing $CrNF$ as a soft ferromagnet versus hard magnetic CrO_2 . Herein we extend the investigation to the study of $CeNCl$ and propose the hitherto unidentified $CeNF$. Particularly the structure of $CeNCl$ is revisited by complementing the partial early determination [7] with calculated positional parameters of Ce and Cl and providing a description of its electronic structure and bonding properties. Further, based on $ThNF$ former works, a proposition of a ground state structure for $CeNF$ is given from energy quantities determined for two model structures: rhombohedral *versus* tetragonal.

For these objectives we used two computational methods within DFT: The VASP code with PAW (projected augmented plane wave) method [15,16] allows geometry optimization, ground state energies and analyses of the charge density. Then the full analysis of the properties of the electronic structure and chemical bonding properties based on the overlap populations (COOP criterion) was done using full potential scalar-relativistic augmented spherical wave (ASW) method [17]. The PBE generalized gradient approximation (GGA) functional [18], accounting for the effects of exchange and correlations within DFT, was considered in all calculations. In spite of the localized f character of cerium, the calculations did not require using GGA+U schemes for better results. For details on the methods the reader is referred to the theoretical development in a review [19].

2. Crystal chemistry and discussion.

Like ThNX ($X = \text{Cl, Br, I}$), CeNCl crystallizes in tetragonal PbFCl-type structure with $P4/nmm$ space group. The structure sketched at Fig. 1a is characterized by layer like $[\text{CeN}]_n$ with nitrogen atoms forming a square lattice. Short Ce–N bonds, likely to exhibit covalent character, are opposed to longer Ce–Cl bonds. $[\text{CeN}]_n$ sheets are separated by puckered chlorine double layers and Ce is found in a monocapped square planar antiprism $\{\text{N}_4\text{Cl}_5\}$ formed by four equatorial Cl ($\text{Cl}_{\text{eq.}}$) and one apical Cl ($\text{Cl}_{\text{ap.}}$).

For $X = \text{F}$ characterizing $\text{Th}^{\text{IV}}\text{NF}$, the structure is rhombohedral with $R\bar{3}m$ space group. Oppositely to PbFCl-type, it has a rather three dimensional structure whose projection in hexagonal symmetry (6 atoms of each species, i.e. 3 times more than in rhombohedral symmetry) reported for Ce case under focus here, is shown in Fig. 1b. The rare earth is surrounded by 4 N and 4 F (see the bonds around Ce designated by '1') forming a distorted cube due to longer Ce–F versus shorter Ce–N (cf. Table 2).

The difference between the two structures shows that dimensionality is a key parameter driven by the nature of the halide: Chlorine is a big anion and subsequently largely polarizable ($\alpha = 2.18 \text{ \AA}^3$) [20]. It tends to reduce its negative charge by polarizing (distorting its electron cloud) towards the cation (Ce), whence the layer-like conformation as in PbFCl type. On the contrary this cannot be obtained with smaller size fluorine which is much less polarizable ($\alpha = 0.557 \text{ \AA}^3$) [20] and the resulting structure

cannot have a 2D character. This is quantitatively shown with the discussion of the electronic structures.

3. Geometry optimization, energy and electron localization: Results and discussions.

The experimental structure determination of CeNCl provides only a and c tetragonal parameters (Table 1). As shown in Fig. 1a, N is at the origin whereas Ce and Cl are at $(2c)$ particular positions $(0, \frac{1}{2}, z)$ for which we chose as starting trial z coordinates those of ThNCl, i.e. 0.635 and 0.165 for Cl and Ce respectively [13]. The resulting parameters and volume after full geometry optimization are in fair agreement with experiment with nevertheless a trend of a 2 % smaller volume for CeNCl. $z(\text{Ce})$ and $z(\text{Cl})$ are also within range of starting values of ThNCl. The volume of CeNF is found smaller due to the size difference between Cl and F (1.0 versus 0.7 Å). However a more striking feature is the large diminution of the c/a ratio which decreases from 1.73 in CeNCl to 1.55 in CeNF; the consequence is a small difference $d(\text{Ce-F}) - d(\text{Ce-N}) = 0.13$ Å, versus $d(\text{Ce-Cl}) - d(\text{Ce-N}) = 0.88$ Å. Such a result is not due to the radii of atomic N and F which are close in magnitudes (resp. 0.75 and 0.72 Å), but mainly arises from the reduced c/a . This is likely related with the probable instability of CeNF in such layer like structure as shown in next paragraph from energy trends. The total energies per 2 formula units (FU) are provided at the last line of Table 1; they are used in next paragraph for a confrontation with the rhombohedral structure energy results.

Although CeNCl is tetragonal as described above, subsequent calculations on both CeNCl and CeNF in the rhombohedral ThNF structure were carried out in order to energy discriminate the trial structures. Table 2 shows the results considering the crystal data of rhombohedral ThNF as starting input [13]. For the nitride chloride, a largely smaller volume is calculated with respect to its experimental one whereas a similar volume magnitude is obtained for CeNF. The interatomic distances are consequently smaller but the difference $d(\text{Ce-Cl}) - d(\text{Ce-N})$ is now 0.63 Å, versus 0.88 Å in the tetragonal structure. The trend $d(\text{Ce-F}) - d(\text{Ce-N}) = 0.24$ Å is larger than in the tetragonal structure.

The last line gives the total energies for the two compounds. A comparison with the energies in Table 1 shows the following trend:

CeNCl: $\Delta E_{\text{TOT.}}$ (tetrag.-rhomb.) = -0.23 eV / cell.

CeNF: $\Delta E_{\text{TOT.}}$ (tetrag.-rhomb.) = +0.65 eV / cell.

CeNCl is stable in its experimentally evidenced ground state tetragonal structure. This validates the calculations in reproducing the experimental structure. More interesting is the large stabilization of CeNF in the rhombohedral structure versus the tetragonal one.

Lastly we have carried complementary calculations testing other structural configurations:

- Calculation of CeNCl in the orthorhombic FeOCl-type adopted by layered nitride halides MNX (M = IVB transition element and X = Cl, Br, I) as discussed in ref. [8]. The energy of the fully geometry optimized structure is then -41.935 eV, i.e. -1.41 eV higher than the ground state structure. Then among the nitride halides tetragonal CeNCl presents unique structural features.
- In view of the three dimensional like rhombohedral CeNF structure and the closer magnitude of $d(\text{Ce-F}) / d(\text{Ce-N})$ with respect of the tetragonal setting, an anionic disorder was considered by redistributing the anions over the four available sites (cf. Table 2). The result is a large energy destabilization by ~ 1.8 eV /cell versus the anionically ordered structure.

The results can be assessed further by analyzing the charge density issued from the self consistent calculations using the AIM (atoms in molecules theory) approach [21] developed by Bader whereby the molecules are partitioned into atoms as based on the electronic charge density whereby it is assumed that in chemical systems, charge density reaches a minimum between atoms. The Bader analysis does not constitute a tool for evaluating absolute ionizations but it is useful when trends between similar chemical compounds are discussed. The results of computed charges Q are such that they lead to neutrality:

rh. CeNF: $Q(\text{Ce}) = + 2.15; Q(\text{N}) = -1.37; Q(\text{F}) = - 0.78. \Delta Q = \pm 2.15$

tet. CeNF: $Q(\text{Ce}) = + 2.09; Q(\text{N}) = -1.28; Q(\text{F}) = - 0.81. \Delta Q = \pm 2.09$

and

rh. CeNCl: $Q(\text{Ce}) = + 1.96$; $Q(\text{N}) = -1.32$; $Q(\text{Cl}) = - 0.64$. $\Delta Q = \pm 1.96$

tet. CeNCl: $Q(\text{Ce}) = + 2.00$; $Q(\text{N}) = -1.29$; $Q(\text{Cl}) = - 0.71$. $\Delta Q = \pm 2.00$

While charge flows from Ce towards N and X in both compounds and structures, the amount of charge transfer does not lead to the formal $\text{Ce}^{+4}\text{N}^{-3}\text{X}^{-1}$. Such a fully ionic character cannot be obtained in the solid state but the respective charges are proportional to the ionic magnitudes, with larger charge on N than X and an overall more ionic CeNF than CeNCl as expected from their respective electronegativities: F ($\chi = 3.98$) and $\chi(\text{Cl}) = 3.16$. The rhombohedral structure of CeNF allows for larger charge transfer from Ce to N and F versus the tetragonal one. The opposite trend is observed in CeNCl in its ground state tetragonal structure. These trends are similar to ThNX cases [13] though with larger charge transfer magnitudes due to difference in electronegativities: $\chi(\text{Th}) = 1.3$ while $\chi(\text{Ce}) = 1.12$. Then besides the energy based criteria above, the rhombohedral structure is preferred for CeNF because it allows larger charge transfer on N ensuring for the strong Ce-N bonding while keeping a constant negative charge on F close to full anionic.

The charge transfers in isoelectronic CeO_2 are calculated for the sake of comparison with the two ternary compounds:

Fluorite CeO_2 : $Q(\text{Ce}) = + 2.24$; $Q(\text{O}) = -1.12$.

With $\Delta Q = \pm 2.24$, the oxide has the largest cation/anions charge exchange. The result lets suggest that the ionic character introduced by X is less effective than the covalent one introduced by N, whence the expectation of strong Ce-N as discussed in next section.

4. Electronic structure and chemical bonding

With the calculated parameters of the ground state structures (Tables 1 and 2), the detailed electronic band structure and chemical bonding properties are obtained using scalar relativistic calculations with the full potential ASW method [17]. The plots for CeO_2 are also presented with parameters from ref. [22]. As above, at self consistent energy convergence the charge transfer is from Ce towards N and X in CeNX on one hand

and from Ce to O in CeO₂ on the other hand, in agreement with the above computed quantities.

Figs. 2 show the electronic band structures along the major directions (x - axis) of the respective Brillouin zones, i.e. tetragonal, rhombohedral and cubic. The energy along the y -axis is with respect to E_V , top of the valence band (VB) in so far that the three compounds are insulating with gap magnitudes of ~ 1.9 eV (CeNCl), ~ 1.8 eV (CeNF) and ~ 2.2 eV (CeO₂). The latter gap magnitude agrees with the insulating character identified by SCF methods [22]. The top of VB is dominated by halogen (oxygen) p states and separated by the band gap from the conduction band (CB) containing mainly Ce empty $4f$ states. However the chemical bonding (quantum mixing) between Ce and X(O) is ensured by the itinerant parts of f , d and p states respectively at the top of VB, as detailed in the density of states (DOS) plots which also address the shape of the bands. The lower parts of the valence bands comprise the low energy lying s -like bands.

Figs. 3 present the site projected DOS (PDOS). They mirror the band structure plots by showing the dominant localized (sharp) Ce states within CB and the broader delocalized states arising from itinerant (red lines) Ce having similar skyline with N- p states (green lines) and less magnitude and similarity with X. These features are encountered in the two panels 3a and 3b. On the opposite less mixing of F- p (blue) can be observed with the rare earth itinerant states. Further they are separated from the Ce-N (red-green) block and found at lower energy in CeNF (Fig. 3b) versus panel 3a (CeNCl) due to the larger electronegativity of F versus Cl. These DOS are mirrored by the non dispersed bands between -4 and -6 eV in Fig. 2b. The mixing between Ce and N is also observed in the lower part of the VB for the s states. Note that the halogen s states, not shown, are found at energies below -13 eV with respect to E_V .

Fig. 3c showing the PDOS of CeO₂ presents similar features with the other panels regarding the position of Ce empty $4f$ states within the CB and the top of the VB dominated by itinerant Ce and O states. This is expected in so far that the three compounds are isoelectronic, meaning that the same numbers of electrons are redistributed over different atomic constituents. The major differences with respect to the nitride-halide DOS arise from the presence of halogen.

The quantum mixing between Ce on one hand and X (O) on the other hand can be further assessed using the COOP criterion based on overlap matrix elements S_{ij} of

chemical bonding [23]. In the plots positive, negative and zero intensities correspond to bonding, antibonding and non-bonding interactions. Figs. 4 show the COOP for pair interactions in CeNCl and CeNF in both ground state rhombohedral and tetragonal forms for comparisons: Ce–N is bonding throughout the VB in all three first panels although a small anti-bonding contribution (negative magnitudes along COOP y –axis) is observed at ~ -1.8 eV in *rh.*-CeNF (panel *b*). However comparing CeNCl and CeNF COOP, it is clear that Ce–N bonding is stronger in the latter, in agreement with the Ce–N smaller separation and the covalent like bonding, contrary to Ce–F larger distance with ionic like bond. These latter are bonding at the energy position of F(*p*) in the DOS plot (Fig. 2b) and presenting more intense antibonding COOPs in the ~ 4 eV energy range below E_v . In hypothetic tetragonal structure of CeNF (Fig. 4c), the bonding Ce–N is largely compensated with antibonding Ce–F, in agreement with the less stability of the compound in such layered structure.

5. Conclusions and prospective synthesis route for CeNF

Based on the fact that the whole ThNX nitride halides exists, with rhombohedral symmetry for $X = F$ and tetragonal for the other $X = Cl, Br, I$, whereas only CeNCl is identified and (partially) experimentally characterized in tetragonal symmetry, we have investigated both CeNCl and hitherto undiscovered CeNF within DFT methodology.

The results complement the early crystal structure determinations of CeNCl and show its stability in the experimental structure, i.e. versus rhombohedral symmetry. This is opposite to CeNF which is clearly identified in the rhombohedral symmetry like ThNF from energy criteria. Similarly to CeO₂, both CeNF and CeNCl are insulating with smaller band gaps thanks to the Ce–N covalent bond. This prevailing bond was also identified from analyses of overlap populations.

The computational results let propose synthetic routes presently under evaluation along two different protocols:

- a- the ‘ammonolysis’ of the fluoride Ce^{III}F₃ precursor such as the protocol used by Schurz et al. for obtaining MNX family [8] or ;
- b- the method using fluorinated fluxes, preferably with nascent fluorine (strongly oxidizing) on Cr^{III}N following a protocol proposed for preparing ZrNF [5].

The latter protocol seems relevant from the electronic structure characteristics of CeNF, whereby within CeN [24], covalent Ce–N bonding is expected to be modified but still keep prevailing as shown from the COOP analysis upon introducing fluorine. Lastly the reaction $\text{CeN} + \frac{1}{2} \text{F}_2 \rightarrow \text{CeNF}$ is calculated favorable for synthesis with negative enthalpy of ~ -1.6 eV/at.

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Table 1.

CeNCl and CeNF in PbFCl-type structure ($P4/nmm$): Calculated and (experimental) lattice and atomic parameters in tetragonal symmetry. Unchanged N position at origin (0, 0, 0). FU: formula unit. Starting parameters for CeNF are those of CeNCl.

$P4/nmm$ ($Z = 2$ FU)	CeNCl	CeNF
a (Å)	4.01 (4.079)	3.797
c (Å)	6.93 (6.837)	5.881
V (Å ³)	111.4 (113.76)	84.79
Atoms at $(2c)$ 0, $\frac{1}{2}$, z		
z_{Ce}	0.166 (-)	0.203
z_{Cl}	0.628 (-)	0.605
$d(\text{Ce-N})$ (Å)	2.30 (2.33)	2.24
$d(\text{Ce-X})$ (Å)	3.18 (3.20)	2.37
Energy (eV)	-43.34	-47.13

Table 2

CeNCl and CeNF in rhombohedral $R\bar{3}m$ ThNF structure: Calculated lattice and atomic parameters with ThNF starting parameters.

N.B. $a_{\text{hex.}} = a_{\text{R}}\sqrt{2(1-\cos\alpha)}$; $c_{\text{hex.}} = a_{\text{R}}\sqrt{3(1+2\cos\alpha)}$, i.e. $a = 3.878$ Å, $c = 19.928$ Å

$R\bar{3}m$ ($Z = 2$ FU)	CeNCl	CeNF
a (Å)	8.51	7.01
$\alpha_{\text{rh.}}$	27°01'	32°12'
V (Å ³)	102.50	84.82
Atoms at $(2c)$ x, x, x		
X_{Ce}	0.223	0.261
X_{N}	0.378	0.377
X_{F}	0.132	0.131
$d(\text{Ce-N})$ (Å)	2.20	2.37
$d(\text{Ce-X})$ (Å)	2.82	2.61
Energy (eV)	-43.11	-47.78

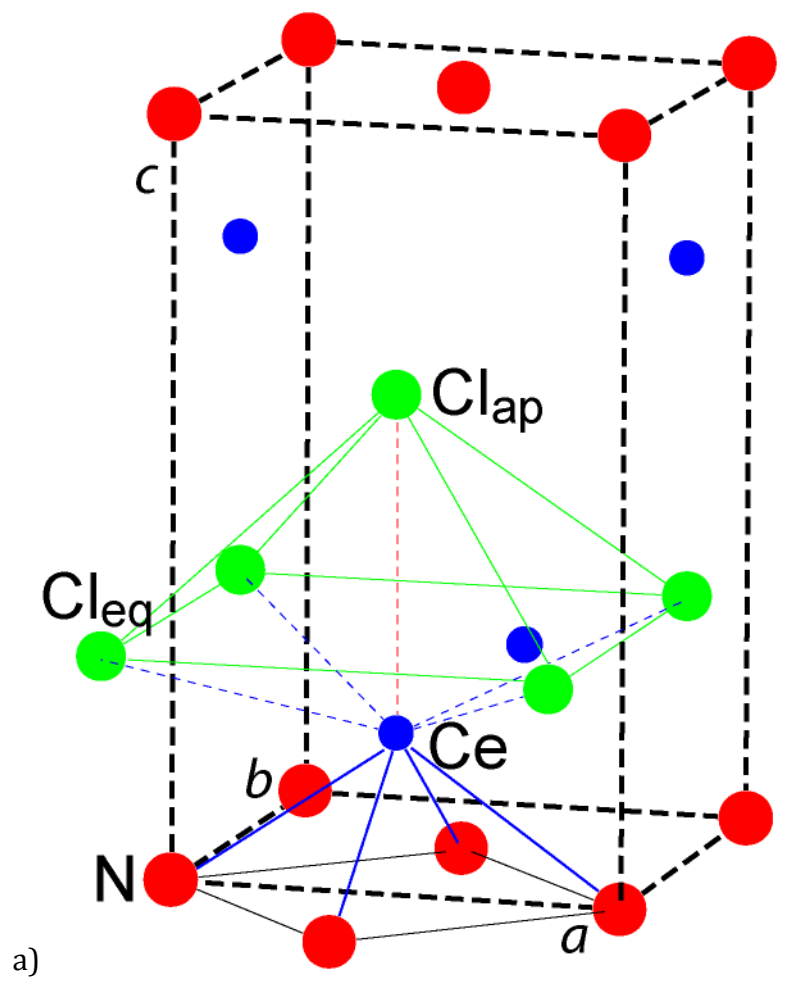
FIGURES

Fig. 1. Tetragonal CeNCl and rhombohedral CeNF ground state structures.

Fig. 2. Electronic band structure along major respective Brillouin zones of CeNCl, CeNF and CeO₂.

Fig.3. Site projected DOS for CeNCl, CeNF and CeO₂.

Fig. 4. Chemical bonding for pair interactions in CeNCl, CeNF and CeO₂.



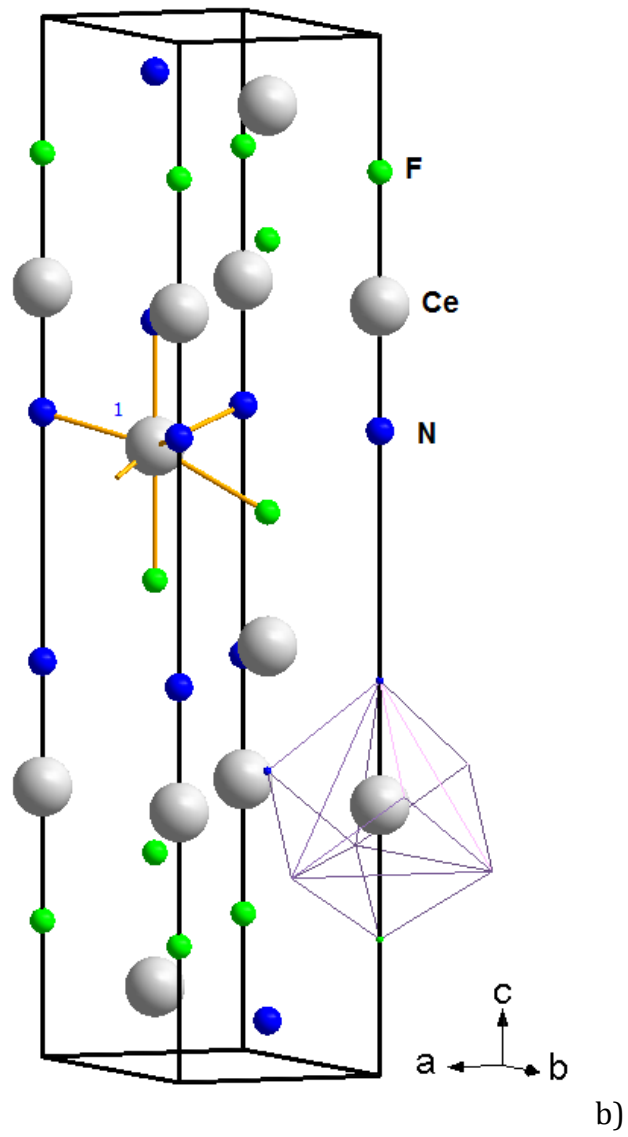


Fig. 1.

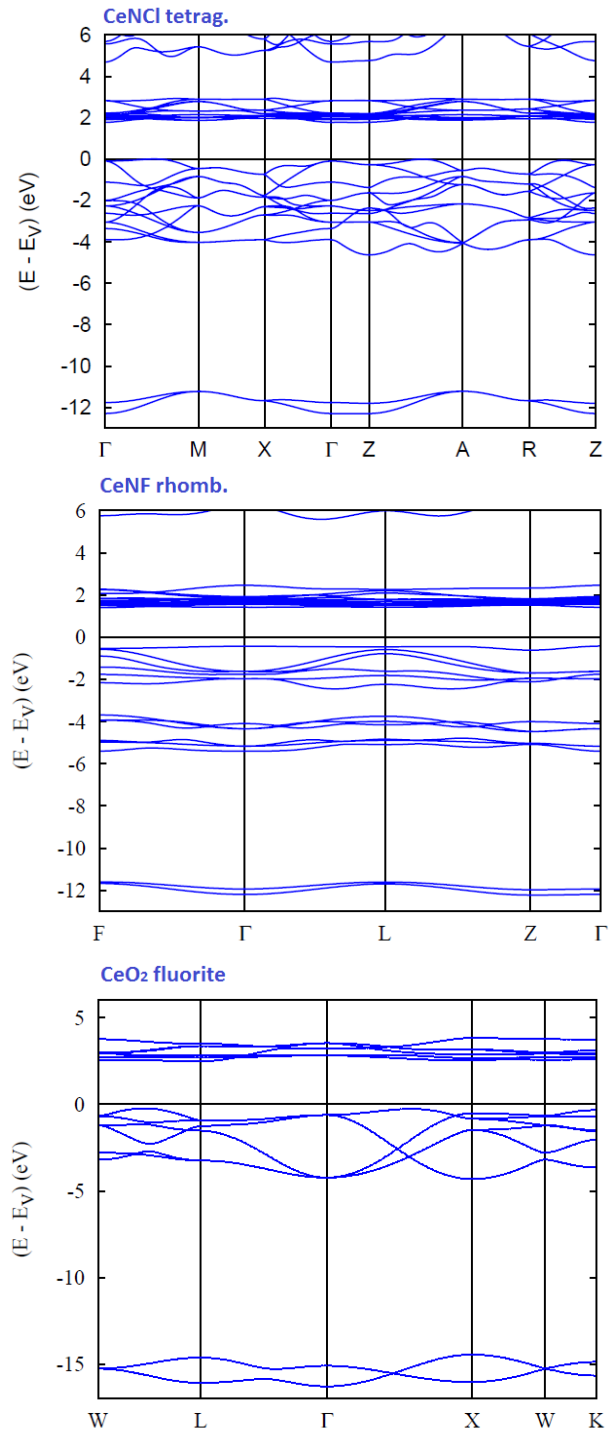


Fig. 2

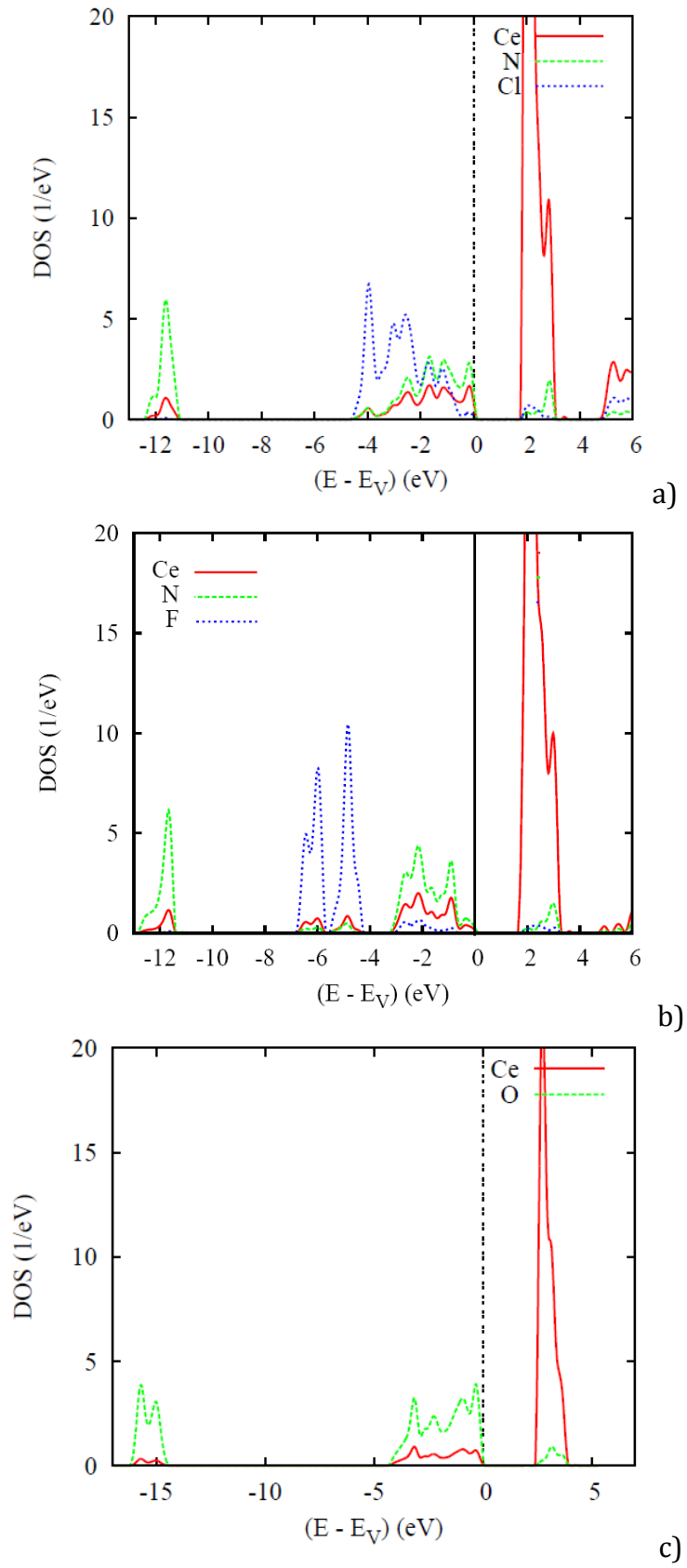


Fig.3

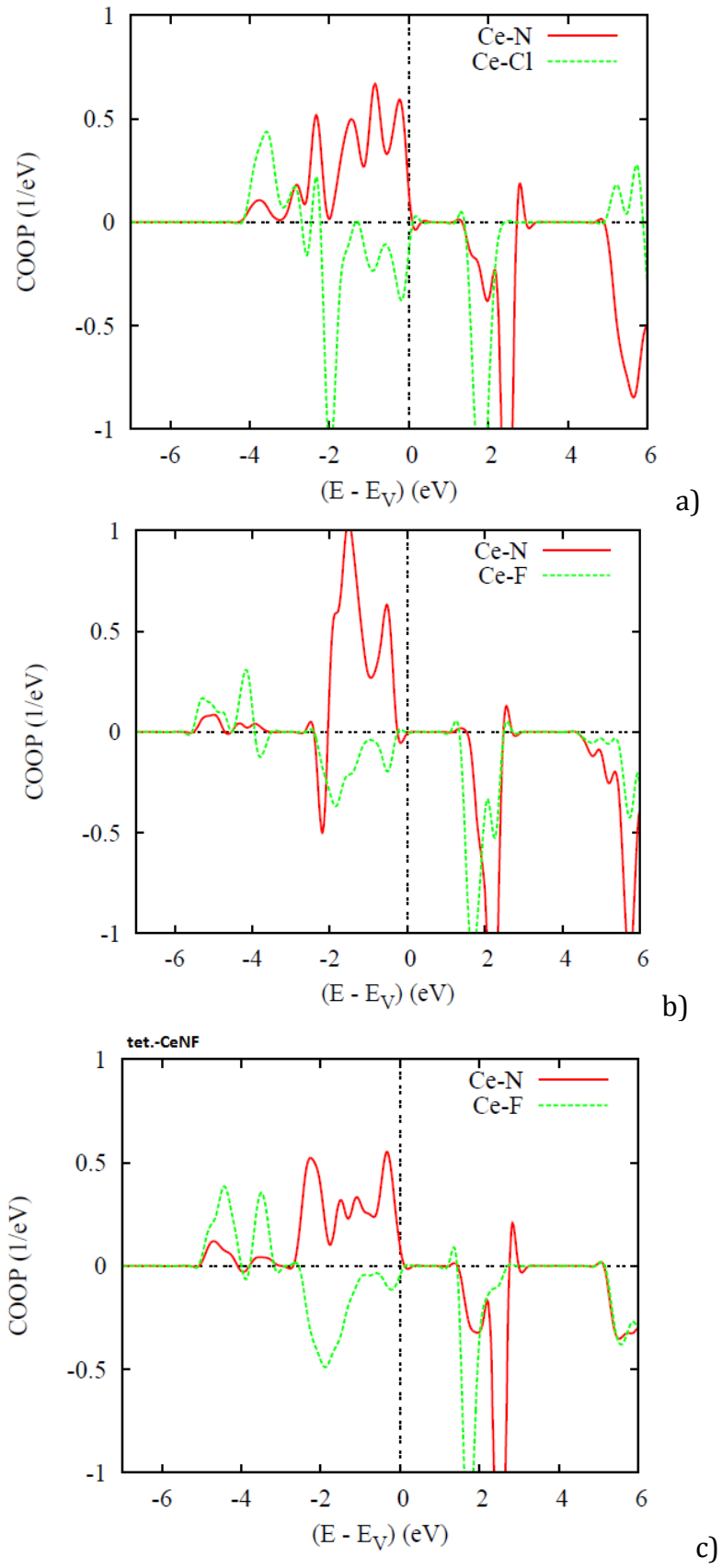


Fig. 4.