



The displacement effect of a fluorine atom in CaF₂ on the band structure

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ABSTRACT

We obtained the results for each configuration [100], [110] and [111] and each configuration contains two atoms of calcium and four fluorine atoms with lattice type B. This study was made by a code that is based on the DFT called wien2k. The results obtained are in good agreement with the experiment. For CaF₂, an important variation of the fluoride ions concentration in CaF₂ after displacement has been observed on the map of e-Density. The interpretation of the results is based on the existence of an important number of defects which are created by changing the atomic positions inside of sub lattice.

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1. Introduction

It is known that X-irradiation at 77 K produces two main absorption bands at about 385 and 433 nm. These absorption bands have been identified as due to FA centres [1,2]. Very recently, Rauch [11] has investigated the effect of bleaching at 77 K with 385 nm light the spectrum. According to his results, during this bleaching, a new centre is formed with absorption bands at 440 and 325 nm, its emission (peaking at 635 nm) being polarized along the [100] directions. He argues that this spectrum should belong to an F₂A centre, produced by ionization of what he

assumes are F₂A centres. His results, however, can be better interpreted assuming that this new centre is, in fact, a F₂A centre created by trapping at an F₂A centre an electron released from another F₂A centre. This mechanism would explain his experimental results, mainly the point that cannot be fully understood with his model: the new centres are created randomly oriented across all the space directions. Moreover, this interpretation accounts for the other experimental results (low-temperature X-irradiation, dichroism, the growth of the concentration of the Y centre during the thermal decay of these new centres). Other absorption bands at 322, 385, 500 and 600 nm (1) are created by X-irradiation at room temperature. Those at 322, 385 and 600 nm were early reported by Scouler and Smakula [3]. The substrate at room temperature diffracted by X-ray leads to formation

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fluorine ions F-F in the same direction of the incident beam on the surface during the first nanosecond of diffraction. the vacancy defects are formed with the emission of light of a second electron study also shows that the structure conserve its external form throughout diffraction and Anion mobility is much greater than that of interstitial defects [4]. Despite several decades of investigation into the problem of colloid growth in the bulk [5] of alkaline-earth halides by optical spectroscopy [6] and transmission electron microscopy [7], the structure and spatial distribution of surface colloids is not well understood. Electron-beam excitation of CaF₂ results primarily in valence electron-hole pairs, which form the self-trapped exciton (STEs) with very high efficiency. For high current densities, electron-stimulated surface metallization is determined by an interplay between surface erosion due to the primary beam of electrons, surface diffusion, and the release of fluorine gas. In the initial stage, surface diffusion of F centres or fluorine vacancies leads to a formation of small colloids randomly distributed over the surface. Continued irradiation leads to growing colloids but also to the formation of large-area metal films pressurized by fluorine gas emerging from the bulk [8]. Experimental characterization of such fundamental defects as [F and H]-centers, and self-trapped holes (STH) can be dated by late 1960s [9]. Calcium fluoride, as well as other alkaline-earth fluorides with the same structure, is known to have the low colour ability at room temperature upon the exposure to ionizing radiation. This is closely related to the fundamental mechanisms of exciton relaxation and the formation of F-H pairs which are not fully understood despite the long going research. In 1979 Catlow [10] has formulated several questions concerning these processes. The main obstacle for industrial use of CaF₂ is the inevitable presence of oxygen centres, which have optical absorption in the VUV region. Again, two different models have been proposed for this centre (the X centre). Rauch [11] and Arkhangelskaya and Shcheulin [12] propose a linear F3A centre in view of their results of polarization luminescence. Doualan et al. [13] tentatively propose an F2A centre. Both models are compatible with other results. This result, however, leaves out other possibilities such as an F2A or 2A an F3A centre. At 300 K, the spectrum corresponding to the Y centres is formed. If the X centre were an F2A centre, we would expect the formation of F2A centres if the F2A centre were ionized during the bleaching. The purpose of this paper is the theoretical investigation of perturbed F-centers in CaF₂ crystals by means of ab initio calculation.

2. Computational method

The calculations were performed using DFT [14] based on FP-LAPW method [15], as implemented in WIEN2K package [15]. The electronic exchange–correlation potential is described with the local density approximation (LDA) [16]. The wave function expansion inside the muffin tins is taken up to $l_{\max} = 10$. The core energy cut off is taken as -6.0 Ryd. The k-point sampling in the irreducible part of the Brillouin Zone (BZ) is performed using $(8 \times 8 \times 8)$ Monkhorst–pack grid. All structures are fully relaxed until the forces on the atoms are less than 2 m Ry/a.u. The convergence of the self-consistent calculations is taken with respect to the total charge of the system with a tolerance of 0.0001 electron charge. All lattices constant are obtained by optimizing the structure using the Murnaghan equation of state [17]. All calculations of CaF₂[100], CaF₂[110] and CaF₂[111] in different configurations, the different parameter for each structure were held in Table 1. For each case, equilibrium lattice parameter was obtained by minimizing the total energy with respect to the cell volume. All electronic properties, such as the DOS, and energy bands, were then calculated for the equilibrium lattice parameter.

Table.1

Details of calculate structure for three configurations.

Configuration	CaF ₂ [100]	CaF ₂ [110]	CaF ₂ [111]
Lattice parameter (Å°)	a = 6.11(Å°)	a = 5.58(Å°)	a = 5.42 (Å°)
Ca1	0 0 0	0 0 0	0 0 0
Ca2	0.5 0.5 0	0.5 0.5 0	0.5 0.5 0
F1	0.25 0.25 0.25	0.25 0.25 0.25	0.25 0.25 0.25
F2	0.75 0.75 0.25	0.75 0.75 0.25	0.75 0.75 0.25
F3	0.5 0.75 0.25	0.5 0.0 0.25	0.5 0.0 0.5
F4	0.75 0.25 0.25	0.75 0.25 0.25	0.75 0.25 0.25
β (GP)	46.77	72.99	88.55
β'	3.57	4.52	4.25
Energy (Ry)	-3510.384576	-3510.495904	-3510.642946
Distances between atoms neighbour (Å°)	d[F1-F2] = 3.05	d[F1-F2] = 2.80	d[F1-F2] = 2.71
	d[F3-F2] = 1.52	d[F3-F2] = 1.97	d[F3-F2] = 2.35
	d[F3-F4] = 5.51	d[F3-F4] = 1.97	d[F3-F4] = 2.35
	d[F1-F3] = 3.42	d[F1-F3] = 1.97	d[F1-F3] = 2.35
	d[F1-F4] = 3.05	d[F1-F4] = 3.41	d[F1-F4] = 2.35
	d[F1-Ca] = 2.64	d[F1-Ca] = 2.41	d[F1-Ca] = 2.35
	d[F2-Ca] = 2.64	d[F2-Ca] = 2.41	d[F2-Ca] = 2.35
	d[F3-Ca] = 2.16	d[F3-Ca] = 3.12	d[F3-Ca] = 2.71
d[F4-Ca] = 2.64	d[F4-Ca] = 2.41	d[F4-Ca] = 2.35	

3. Results and discussion

3.1. Structural properties

This study was conducted by the technique of super cell that is implanted in wien2k. To simulate this experiment as a thin layer we choose a super cell with six atoms in a lattice type B and to realize this work we break the symmetry of the cell which an atom of fluorine chooses his position with all atoms after displacement (see the Table 1). The second step we optimize the structure for each configuration. We begin by making a comparison of structural stability for three configurations [100], [011] and [111]. The total energy as a function of volume per formula unit of CaF₂ {[100], [110] and [111]} is shown in Fig. 1. It shows that the CaF₂[111] structure has lower energy than the CaF₂[100] and CaF₂[110] structure. Our results are good agreement with other results [18–20].

There is a big drop in the value of the equilibrium lattice parameter with its energy after the displacement an atom of fluorine following different directions from x to z for each configuration the results shown in Table 1. with other funding such as the bulk modulus and his drift. Reading the data after the fitting curves with Murnaghan equation of state [21]. Table 1 also, summarizes the modal contact distances and average coordination numbers for different atoms of fluorine. The values obtained for modal bond distances are compared with those obtained by other that exist. The distances d[F2-F3] of CaF₂[100] and d[F1-F3] with d[F4-F3] of CaF₂[110] are significantly lower than coordination numbers in the crystalline state perfect because of defects training or vacuum that pushes sub-lattice of atoms to rearrange themselves again and form islands of atoms. To our knowledge, this is the first time we get the results shown in the table.

3.2. Electronic structure and the band gap calculations

3.2.1. CaF₂[100]

The presence of the vacuum site in CaF₂ means that F must exchange place this is shown in Fig. 2(d-h-l) with jmol-code. The calculated electronic band structure of CaF₂[100] configuration shows the conduction of band minimum (CBM) which is situated at the center of the BZ and the valence band maximum (VBM) is located at H symmetry points of the BZ. Fig. 1a. shows clearly two bands superimposed one over the other β and α almost the same energy of two atoms F2 and F3 cross Fermi level at H point,

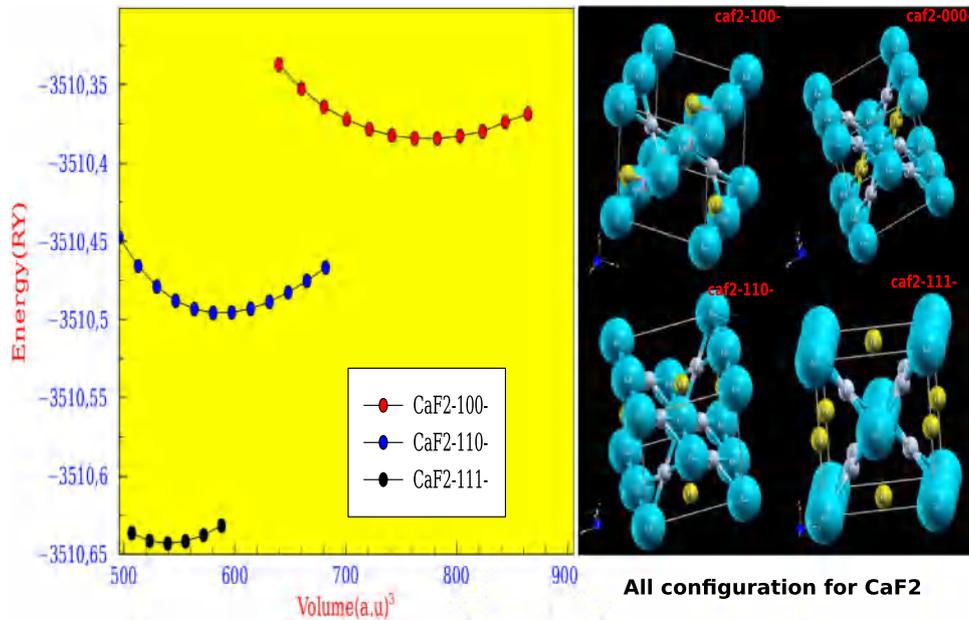


Fig. 1. Energy as a function of volume for each configuration.

so the metallic character of the configuration CaF2[100] appear clearly in our figure. It is clear that upper of (VB) dominated by 2p fluorine atomic orbitals and lower (CB) with his three vacancy states dominated by 4s of Ca. On the other hand, displacement b band of F2 and F3 below in (VB) leads a loss-energy. To identify the contribution of each orbital in CaF2[100] atoms we investigate the angular momentum decomposition of the atoms projected density of states (PDOS) as represented in Fig. 1b. we will investigate the contribution of each F atom in CaF2[100] configuration. The upper valence bands are formed by two peaks almost of the same energy, α -px-F2 and α -px-F3 the lower peak formed by β -px-F2 and β -px-F3 the middle of the (VB) is formed by bands F1 and F4 with intense peaks pz dominant by F1 atom. In the energy region from -8.0 eV up to Fermi level, a strong polarization exists between all states may lead to forming a covalent bonding between F2-F3 and vacuum. We have examined the electronic charge density of CaF2[100] configuration to depict the bonding properties. The displacement effect of a fluorine atom in CaF2 on the band (see figure e-density illustrated the map of charge density contour in (1 0 1) crystallographic plane which represents all atoms of fluorine and the vacuum represented with jmol code. It is clear that F2 atom show strong covalent bonding with F3 and the rest of fluorine atoms share very weak covalent bonding between them. The vacuums take a single direction along x axis. In all studies of CaF2 atoms were found to shift away from the ideal fluorite site toward the other site, as observed in the structure obtained by diffraction X-ray [22]. The irradiation of insulating crystals with MeV ion beam induces strain and damage nearer the surface [22]. On the other hand, an expansion in the lattice parameter has been seen [22] and becomes completely amorphous. The formation of fluorine vacancies in calcium fluoride is accompanied by the formation of fluorine-rich defects, including H and I centres. The H centre corresponds to a fluorine atom moving in the direction "x" in this studies equivalent to an F2 ion occupying a fluorine lattice site, while the I centre is an F2⁻ ion at an interstitial site. Some fluorine may occupy interstitial sites as neutral atoms or molecules [23] (see Fig. 2).

3.2.2. B-CaF2[110]

Fig. 2 of fat band provides out a window from -8 eV until 14 eV which may give an illustration for all level-energy, in both areas

valence and conduction. Moreover, we can observe on both P-DOS and band structure, the valence band is characterized by a larger dispersion of p states of atoms fluorine in CaF2[110] configuration while the two low conduction bands characterized by p-F3 atom. For both structures, CaF2[100] and CaF2[110] the bottom of the conduction band is dominated by the mixed band's calcium and Fluorine quantum states the upper band valence dominated by α -px and α -py of F3 other bands px and py of F3 and F2 are positioned at the middle of (BV). The presence of some concentrations of vacancies is very clear on the map of e-density and to mimic the real system, the vacancy was formed in the super cell by displacement the fluorine atom in the direction [110]. The same strategy was used for the last configuration. As already analysed in our previous studies the VB and CB are mainly defined by the bonding character. In this configuration, we have seen a transition the band β -P at -8 eV in the last configuration to 1,5 eV whereas, these transitions can be understood as perturbed of F-center that change its form and its size. whilst, the dissociation of fluorine ion allows the Band β to move upwind of the band α . On the other hand, this occupation allows the sub-lattice to arrange for a second time and changes its positions meaning the distances between its closest neighbours vary (see Fig. 1).

However, when the ions are displaced from their ideal lattice sites, this symmetry is broken and polarization appears in the form of superimposed states. Other literature has shown, the inclusion of ion polarization greatly influences the degree of Frankel defect formation and so, in fluorite systems, controls the temperature at which superionicity develops [25,26]. To emphasize the differences in the two models, Fig. 3. show the sum of two atoms which formed an ion and the second figure shows the dispersion terms for forming an island of atoms this situation is an intermediate phase through which the formation of Frankel defects triggered to a strong minimum in the potential energy curve. In this configuration, the material retains almost all of its electronics properties as the previous configuration.

3.2.3. C-CaF2[111]

Fig. 2c clearly shows the fluorine atom that places oneself between the two atoms of Ca, another location of fluorines atoms are located at the cube surface, inter alia the rest of atoms of fluorine are rearranged in a random manner with the vacuum which

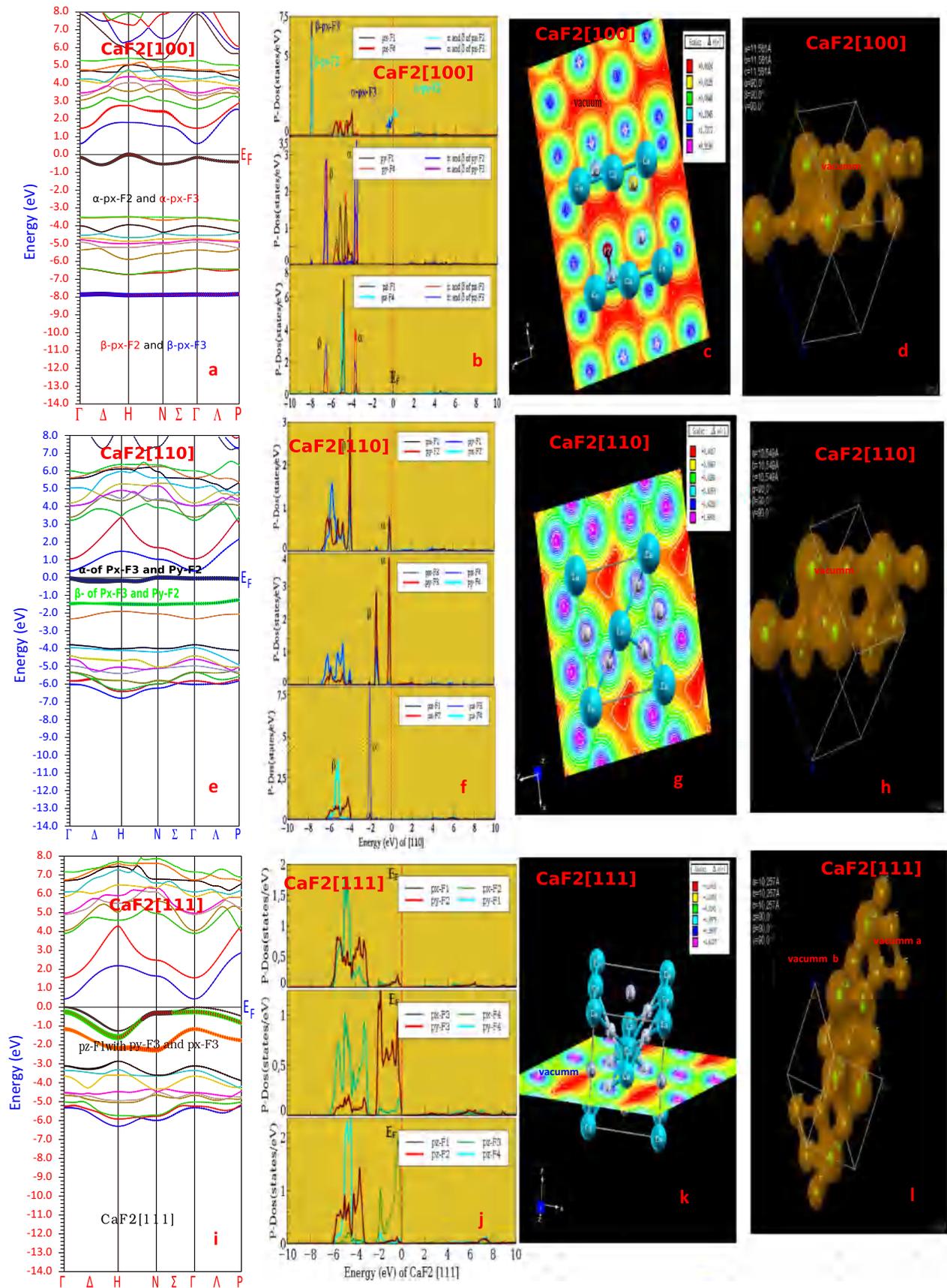


Fig. 2. B S, P-dos and e-Dens for three configurations.

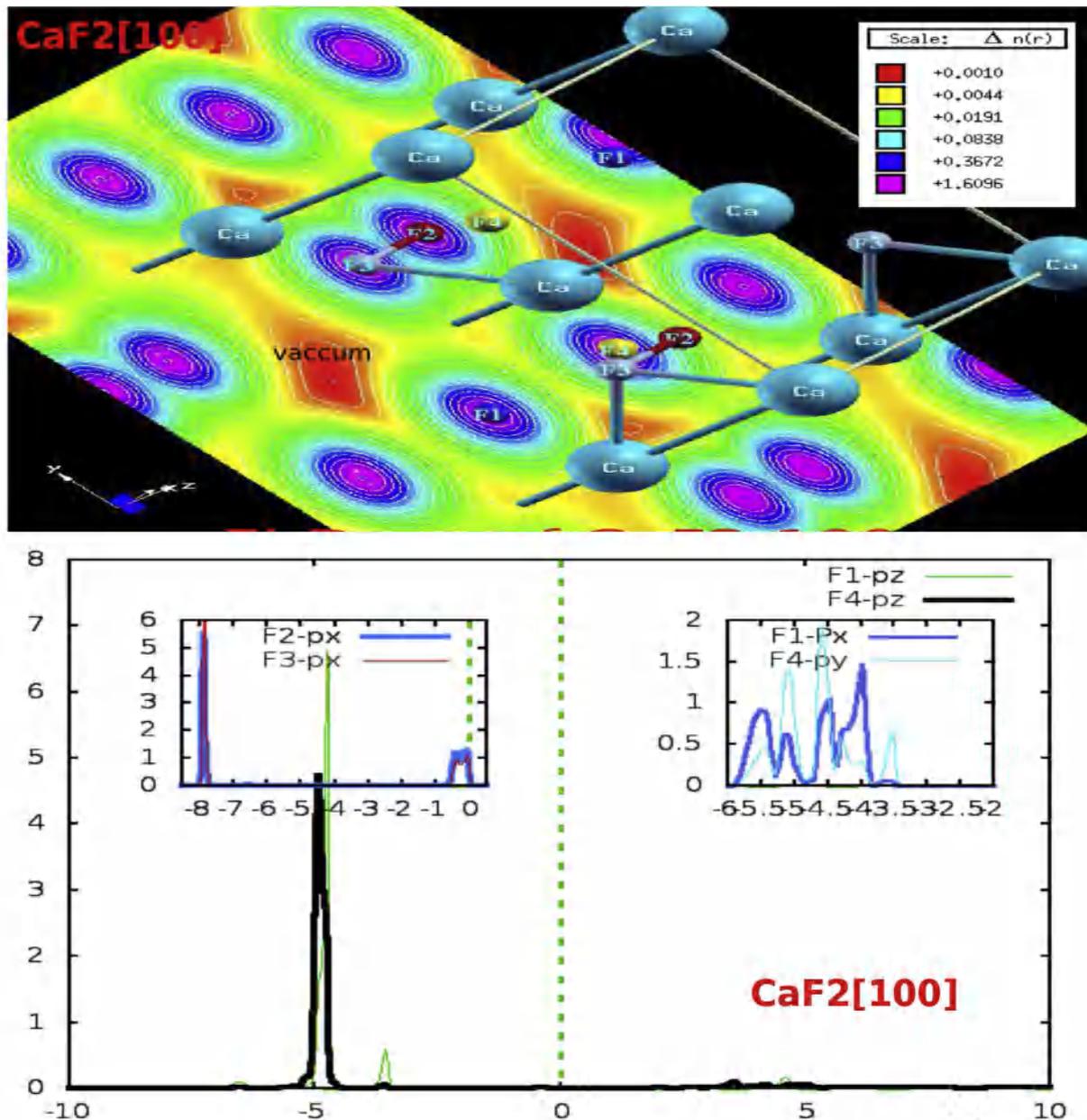


Fig. 3. e-Density and P-Dos of CaF2[100]

appears clearly on the map, so the symmetry is broken of sub-lattice. The symmetry breaking has a larger impact on the F sublattice than on the lattice of Ca. The new ⟨F-F⟩ distributions in sub-lattice become evenly distributed upon the new lowering of the symmetry that leads to an end to a reduction in energy and generates larger islands with two defects the first follows [100] direction and the second follows the direction [110] see Fig. 2g. On the other hand, the both vacuums area in [111] are a small if we compared to the area accumulation of fluorine atoms inside the cube and the decrease of concentration of fluoride ions on the surface was observed but it exist two different types of vacuum the first is horizontal and the second is vertical [24] as such show Fig. 2i. In this configuration, the metallic electronic structure was obtained as two previous configurations. We found that a clear band gap appears in these arrangements only when the local distortion is appropriately included. The P-DOS shows clearly the upper (VB) is a mix of the three levels of ⟨p⟩ atom F3 and, the all conduction band are dominated by s of atoms Ca. The

superposition of the bands near the Fermi level is clear dominated by the states P the metal character only appears that the atom of fluorine leaves its place leaving two types of vacuum. The displacement of the deep bands of the valance band corresponds to Loss of energy in the form of heat or radiation.

4. Conclusion

We presented at first a discussion of the geometry optimization and extracted the lattice parameters as well as the bulk modulus, its derivative and total energy for all three configurations. The major results of this study can be summarized as follow: (a) within the [111] configuration, the [111] arrangement was found to be favourable stable with low energy and The symmetry breaking and local distortion have a larger impact on the F sub-lattice than on the Ca lattice. All vacuum have been successfully obtained for all three configurations and the bonds are illustrated on the table. The variation in shape and size of defects for the three

configurations leads to a reality that the vacuum is not the same. Fig. 3 shows the plots of charge density around the first neighbour atom and the second nearest neighbour atom to a vacancy. There appear accumulation atoms between vacuum sites. Also, the difference in electron density is more or less negligible for the regions between the nearest-neighbor atoms accumulated. The vacancy is thus efficiently screened, similar to what has been previously observed in other jobs. These vacuum pushes neighbouring atoms of sub-lattice to make the strong and weak-links or forms the islands as we have seen on figures (1-c-g-k). The equilibrium lattice parameter for the three configurations were used to calculate the electrical properties. The three figure band structure shows the evolution of energy for (F) sub-lattice, the double and threefold states that cross Fermi level have been dominated by p state and the lower energy of (CB) dominated by s and p of Ca. The displacement the P state toward the top of (VB) over time for three configurations participate in the stability of the material and low energy levels obtained in the conductive part is underestimated due to the approximation LDA, may be this levels are much higher.

References

- [1] V.M. Lisitsyn, V.F. Shtanko, *Opt. Spectrosc.* 42 (1977) 433.
- [2] J.L. Doualan, J. Margerie, F. Martin-Brunetiere, E. Rzepka, *J. Physique Lett.* 44 (1983) L-375.
- [3] W.J. Scouler, A. Smakula, *Phys. Rev.* 120 (1960) 1154.
- [4] J.D. Pistre, Y. Danto, J. Salardenne, Laboratoire de Recherches en Electrotechnique et Physique du Solide B. Saboya et J. F. CHEMIN Centre d'Etudes Nucléaires de Bordeaux-Gradignan (C. E. N. B. G.) Université de Bordeaux I, Domaine Universitaire, 33405 Talence, France (Reçu le 13 juillet 1977, révisé les 24 octobre 1977, 23 décembre 1977, 13 janvier 1978, accepté le 18 janvier 1978).
- [5] A.E. Hughes, S.C. Jain, *Adv. Phys.* 28 (1979) 717.
- [6] S.D. McLaughlin, H.W. Evans, *Phys. Status Solidi* 27 (1968) 695.
- [7] L.E. Murr, *Phys. Status Solidi A* 22 (1974) 239.
- [8] M. Reichling, R.M. Wilson, R. Bennowitz, R.T. Williams, S. Gogoll, E. Stenzel, E. Matthias, Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany and Department of Physics, Wake Forest University, Winston-Salem, NC 27109, USA.
- [9] W. Hayes, J.P. Stott, *Electron nuclear double resonance of the F-centre in CaF₂*, *Proc. Roy. Soc., A* 301 (1967) 313–326.
- [10] C.R.A. Catlow, *Radiation damage and photochromism in the alkaline-earth fluorides*, *J. Phys., C* 12 (1979) 969–988.
- [11] R. Rauch, *Izv. Akad. Nauk. S.S.S.R., Ser. Fiz.* 37 (1973) 5.
- [12] V.A. Arkhangelskaya, A.S. Shcheulin, *Opt. Spectrosc.* 50 (1981) 629.
- [13] J.L. Doualan, J. Margerie, F. Martin-brunetiere, E. Rzepka, *J. Physique Lett.* 44 (1983) L-375.
- [14] W. Kohn, L.J. Sham, *Phys. Rev.* 140 (1965) A1133.
- [15] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnika, K. Luitz, WIEN2k. Technical Universität Wien, Austria, ISBN 3-9501031-1-2, 2001.
- [16] J.P. Perdew, Y. Wang, *Pair-distribution function and its coupling-constant average for the spin-polarized electron gas* *Phys. Rev. B* 46 (1992) 12947.
- [17] F.D. Murnaghan, *Proc. Natl. Acad. Sci.* 30 (1944) 244.
- [18] M. Reichling, R.M. Wilson, R. Bennowitz, R.T. Williams, S. Gogoll, E. Stenzel, E. Matthias, Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany and Department of Physics, Wake Forest University, Winston-Salem, N C 27109, USA
- [19] H. Shi, L. Chang, R. Jia, R.I. Eglitis, *J. Phys. Chem.*
- [20] L. Yue, R. Jia, H. Shi, X. He, R.I. Eglitis, *Phys. Chem. A* 114 (2010) 8444–8449.
- [21] F.D. Murnaghan, *Proc. Natl. Acad. Sci. USA* 30 (1947) 244.
- [22] C.R. WIE, T.VREELAND, Jr. and T.A.TOMBRELLO Divisions of Physics, Mathematics, and Astronomy, and Engineering and Applied Science, California Institute of Technology.
- [23] R. Bennowitz, M. Reichling, E. Matthias, *Surf. Sci.* 387 (1997) 69.
- [24] I. Nepomnyashchikh, E.A. Radzabov, A.V. Egranov, V.F. Ivashchekin, A.S. Istomin, *Radiat. Eff. Defects Solids* 157 (2002) 715.
- [25] M.J. Castiglione, M. Wilson, P.A. Madden, N.C. Pyper, *J. Phys., Condens. Matter* 11 (1999) 9009.
- [26] N.T. Wilson, M. Wilson, P.A. Madden, N.C. Pyper, *J. Chem. Phys.* 105 (1996) 11209.