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Electronic structure of Eu-doped CaO by density functional theory

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Abstract: We report the *ab initio* calculation of electronic structure of Eu-doped CaO. The obtained results appeared in a very good agreement with experimental data and predicted the existence of a ferromagnetic state for one doped compound. The light doping could induce the electron trapping property and the heavy doping the half-metallic ferromagnetic state.

Keywords. CaO; DFT; electronic structure; ab initio; ferromagnetism.

1. Introduction

Calcium oxide (CaO) is a common chemical compound which is present a lot in the lower strata of the Earth. It is widely used in various fields such as chemical, agricultural and civil engineering industry. In material science, CaO is interested because of its defect-induced optical properties. CaO itself is a wide optical gap semiconductor (~7 eV) [1] and the high-purified material is optically clear [2]. The occurrence of F centers (which are anion vacancies that trap one or more electrons) causes the orange luminescence bands at 500 and 627 nm with lifetime of 3 msec and 1 μsec at 4K respectively [3]. A long-life phosphorescence was also detected with a lifetime of 50 sec at 300 K and 125 sec at 77K and was attributed to the thermo-activated release of electrons from some kind of unidentified impurity centers [3]. M. M. Abraham *et al* [2] have successfully doped a highly purified CaO crytal by two monovalent elements Li, Na and two rare-earth elements Ce, Nd. Monovalence-doped crystals have a faint yellow color while Nd-doped crystal is blue and Ce-doped one is intense yellow. In the rocksalt crystal (Fm-3m space group) of CaO, every ion is at the center of inversion, so the first-order Raman scattering is not allowed, but the present of defects activated the forbidden Raman peaks [4]. The CaO based glasses are highly transparent over a wide range of frequency from the near UV (0.2 μm) to the mid-IR (6 μm) [5,6,7] and exhibit a lower intrinsic scattering loss than of any silica glasses [8,9,10]. Therefore, they should be the brilliant candidates for applications such as laser windows, IR domes, IR optical fiber…

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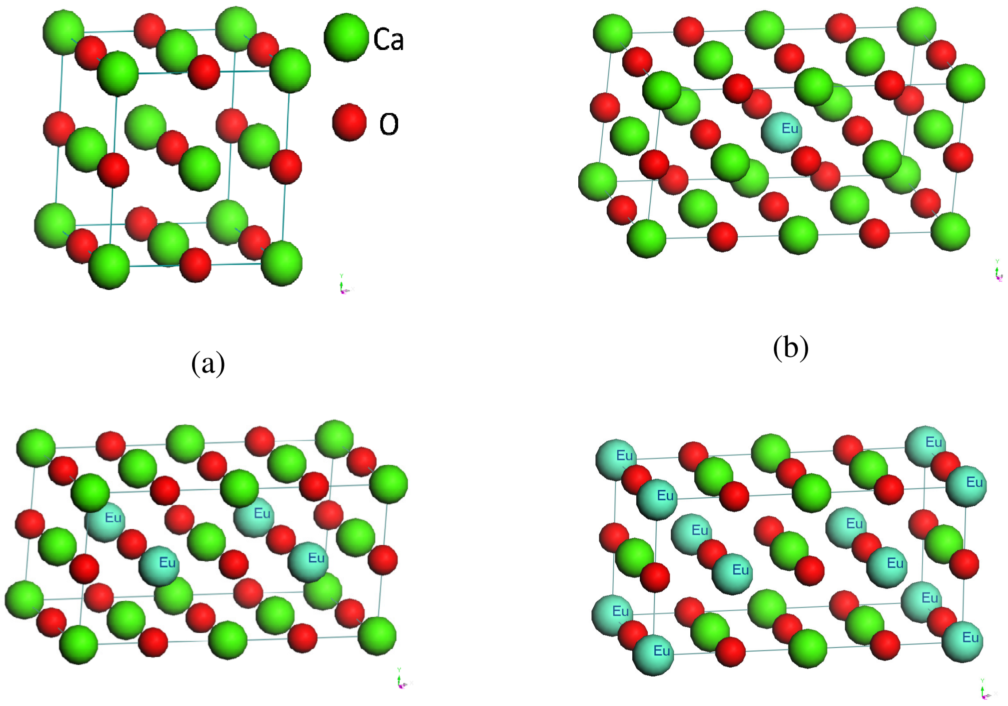
Recently, there was some renewed attention to calcium oxide for its promising applicability in optical memory, spintronics and electronic industry [11,12,13]. Photoluminescent spectra measurements by V.G. Kravets indicated that the Eu, Sm doped CaO have property of electron trapping which make them suitable for the optical recording media with recording radiation at 266 nm and reading one at 1064 nm [11]. On the basis of electronic structure and magnetic property calculation using LDA/KKR method, K. Kenmochi *et al* [12] have proposed a new class of diluted magnetic semiconductors (DMS) based on CaO without transition metal elements. The use of CaO in organic light-emitting diods (OLED) also showed the extension of lifetime of these devices [13].

Despite of great potential for various application of CaO, there was a lack of accurate explanations for many interesting physical characteristics, such as, quantitative aspects of ground state, possible magnetic orderings, optical process etc. In this paper, we investigate the optical, electrical and magnetic properties of Eu doped CaO in the framework of Density Functional Theory. Our results showed the electron trapping property of light doped materials and predicted the ferromagnetic half-metallic ground state of heavy doped materials.

2. Calculation methodology



(a) (b)

(c) (d)

Fig. 1. The rock-salt unit cell of CaO (a); the doped supercells $Eu_xCa_{1-x}O$ for x=0.125 (b), 0.25 c) and 0.375 (d).

The unit cell of CaO is Im3m with lattice parameter *a* ~ 4.81Å [14] (Fig. 1(a)). We constructed a supercell of the size 2x1x1 and substituted the calcium with europium atoms to simulate the doped compound $Eu_xCa_{1-x}O$ for x=0.125, 0.25, 0.375 (Fig. 1(b), (c) and (d)). The atomic orbitals were modeled using the double numerical (DN) basis functions plus the diffuse and polarization functions added, i.e. the DNP basis sets provided in Dmol^3 package [15].

Table 1. Lattice constants *a* (in Å) and band gap values (in eV) obtained from DFT calculation using various correlation-exchange functionals

Parameter			*a*	Band gap	Band width			
					O 2s	O 2p	Ca 3s	Ca 3p
Our results (DNP basis set)	LDA/PWC		4.714	5.5	1.7	2.8	1.4	1.5
	GGA	PW91	4.826	5.0	1.3	2.5	1.1	1.2
		PBE	4.841					
		BLYP	4.841					
Ref. [17] (PW basis set)	LDA/PZ-CA		4.712	3.44	-	2.86	-	-
	GGA/PBE		4.819	3.67	-	2.7	-	-
Ref. [16] (Gaussian basis set)	LDA/DS-VWN		4.70	-	1.37	2.88	0.20	1.44
	GGA/PBE		4.81	-	1.01	2.61	0.14	1.05
	Hybrid/B3-PW		4.79	-	1.21	2.85	0.15	1.22
Experiment			4.81[14]	7.1[1]	0.6[16]	0.9[16], 3[18], 9[22]	0.20[16]	0.5[16]

In all calculations, we chose "all electrons" in core treatment options of Dmol^3 to treat the core electrons in the same manner as the valence ones. For the purpose of choosing the optimal correlation-exchange functional, the structure optimization were carried out using the periodic model with various functionals, including the LDA/PWC and three other GGA functionals (PW91, PBE, PLYP). In acceptable error of band gap value (0.1 eV), we applied a Monkhorst-Pack k-point set of 6x6x6 grid with 216 k-points for a unit cell given in Fig. 1(a), and 3x6x6 grid with 108 k-points for a unit cell given in Fig. 1(b), (c) and (d). The optimized cell parameters, band gap and band width values of CaO are listed in Table 1 together with the experimental and theoretical results from other groups.

As observed, the LDA functional tended to underestimate the lattice constants while the GGA ones often overestimated them. A comparison of our results with those given in Ref. [16] (which used the Gaussian basis sets) and in Ref. [17] (which used the plane wave basis sets) shows that the change in form of basis set did not significantly affect the cell parameters but implied a large changes in band gaps and band widths. The DNP basis set seemed to widen the band gap of material in comparison with the plane wave basis sets. While the PBE O 2s, Ca 3p band widths are quite similar for Gaussian and DNP basis sets and twice as large as the experimental ones (Ref.[16] and [18]), the Gaussian/PBE Ca 3s value is much smaller than our DNP/PBE results and give a better fit to the experimental results [16].

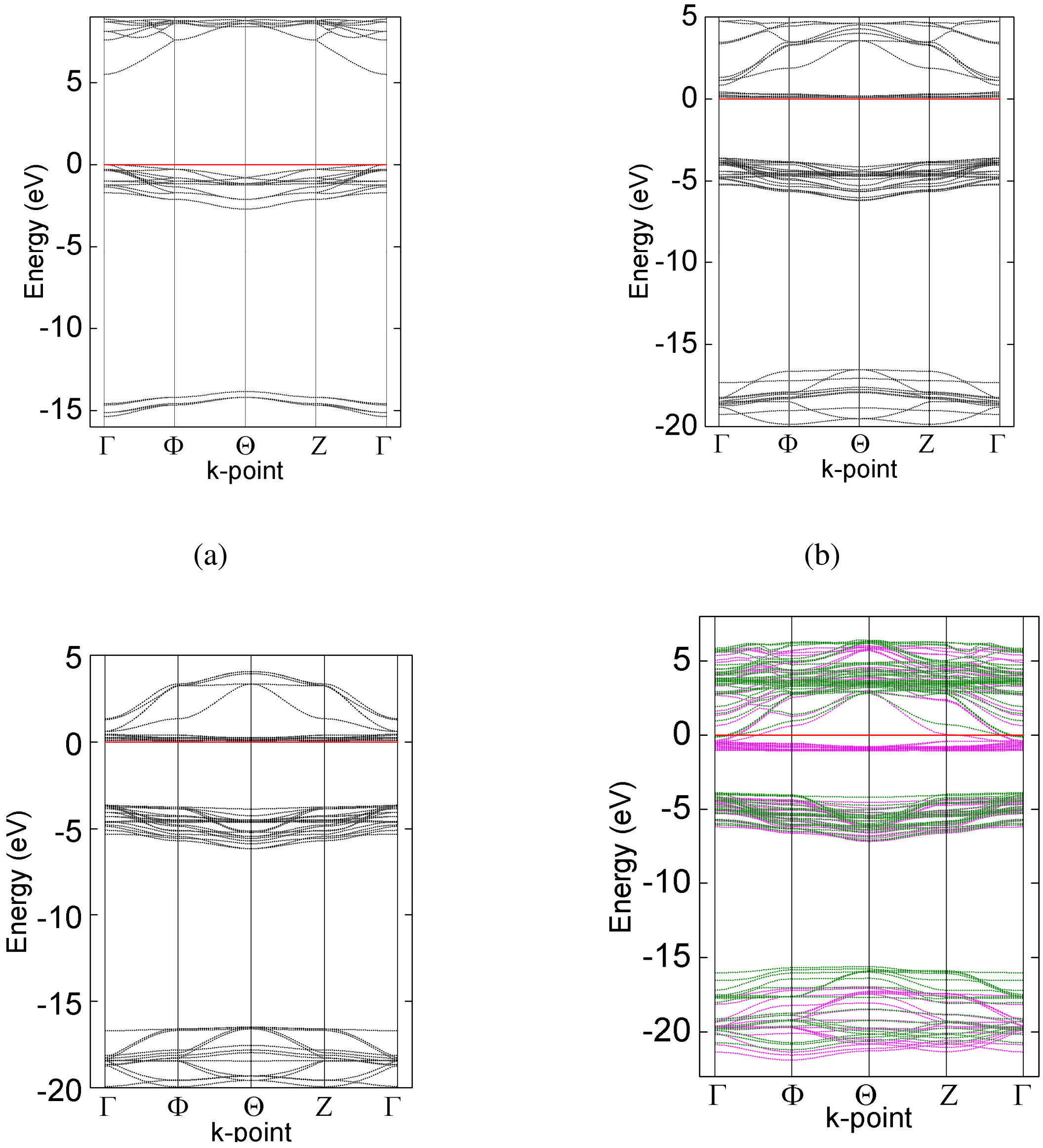
All of the considered theoretical methods underestimated the band-gap. We suggest that the decline from experiment of *ab initio* results may originate from the difference between the real and model structures. It should be noted that the calculated model is idealized to an unbounded crystal without defects. In fact, it is difficult to achieve transparent large indefectible crystals of CaO. Calcium oxide powder, which is composed of micro and nanoparticles, can easily absorb water in the air to become $Ca(OH)_2$. The probability of this reaction is proportional to the total surface area of the powder. Therefore, in CaO powder the rocksalt crystallites often occur in submicro-particles with hydrated coats which cause the powder to be opaque. We remind that the experimental energy band gap of 7.1 eV is yielded from the exciton themorefletance spectrum analysis of a polycrystalline film [1] and the surface hydrolysis was shown to have no significant affect on the spectral features [19]. Despite of this, the band gap widening should occur due to the quantum confinement of the excitons in a small region inside the nanoparticles as possible quantum dots. Even for larger CaO crystals (1 cm^3 [3], 7x7x2 mm^3 [4], 25 cm^3[2], 5cm^3 [20]), there is a number of defect and impurity centers such as F centers [3, 4], Al, Cu, Mg, Mn, P, Si, Sr, Ti impurities [2, 20]. The valence bands of CaO in Ref. [16] were determined via electron momentum spectroscopy (EMS) measured on polycrystal thin films (5 nm in thickness). Although, Auger spectra showed no contamination in the samples, there was probable that some F centers (oxygen vacancy sites) occurred. The oxygen vacancy sites caused the EMS O 2s and Ca 3p bands less dispersive than the *ab initio* ones. The large divergence among experimental O 2p band widths was explained to originate from the difference in preparation routes as well as in sample geometry.

In the following calculation, we utilized the LDA/PWC functional (Perdew and Wang, 1992 [21]) due to the closest match of band gap to experimental value (5.5 eV versus 7.1 eV [1]). The unrestricted DNP/PWC calculations were treated by using the $Dmol^3$ code [15].

3. Results and Discussion

3.1 Ground state of $Eu_xCa_{1-x}O$ for $x=0, 0.125, 0.25, 0.375$

On the purpose of investigating magnetism in Eu doped CaO, we searched for the local minima from various initial ordering states of spins (Eu^{3+} $S=3$), including ferromagnetic, anti-ferromagnetic and non-magnetic state. For $x=0.125$ and 0.25 (light doped materials), all of the results converged to a non-magnetic ground state. But for $x=0.375$, the ground state was found to be ferromagnetic with total spin of Eu^{3+} $S\sim3.45$.



(a)

(b)

(c)

(d)

Fig. 2. Energy band structures of $Eu_xCa_{1-x}O$ at ground state for x=0 (a), 0.125 (b), 0.25 (c), 0.375 (d); the red lines denote Fermi level, which was nomarlized to zero energy.

From band structure analysis (Fig. 2), we suggest that the undoped calcium oxide (x=0) is an insulator with a direct band gap at Γ point E_g=5.5 eV while the light doped materials are non-magnetic semiconductors with indirect band gap E_g=3.7 eV corresponding to the Γ-Θ transition of electrons and the $Eu_{0.375}Ca_{0.625}O$ material is ferromagnetic half-metallic. A brief summary of the ground states under investigation is listed in Table 2.

Table 2. Electrical and magnetic properties of $Eu_xCa_{1-x}O$ (x=0, 0.125, 0.25, 0.375)

x	Electricity	Band gap	Magnetism
0	Insulator	Direct 5.5 eV	Non
0.125	Semi-conductor	In direct (Γ-Θ) 3.7 eV	Non
0.25	Semi-conductor	In direct (Γ-Θ) 3.7 eV	Non
0.375	Half-metallic	------	Ferromagnetic

In the next sections, we discuss in more details about the interesting properties of doped materials, including their electrical, magnetic and optical properties. The obtained results highlight the possibility of application in modern spintronics.

3.2 Light doped CaO ($Eu_xCa_{1-x}O$ with x= 0.125, 0.25)

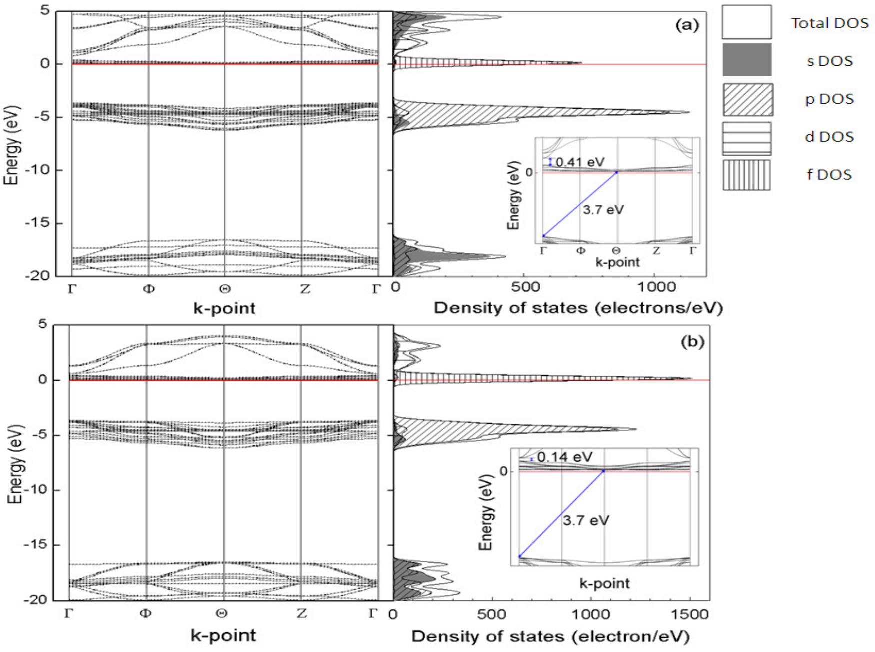


Fig. 3. The ground state band structure and density of states of $Eu_xCa_{1-x}O$ for x=0.125 (a) and x=0.25 (b); the insets enlarge the valence-impurity and impurity-conductive band gaps.

Fig. 3 shows the band structure and the DOS of light doped CaO materials. The Eu impurities contribute a densed and narrow *f*-like band into to the band gap of CaO host lattice and shift the Fermi level up to the bottom of this band. As shown above, these materials are indirect band gap semiconductors. The indirect gap E_g~3.7 eV corresponds to the electron transition from the top of valence band (*p*-like states) at Γ point to the bottom of conductive band (*f*-like states) at Θ point. Because the indirect transition (in which electron absorbs a suitable photon to jump up to conduction band and change its momentum simultaneously) needs to be accompanied by the third particle, the conducting mechanism of the materials should be related to phonon.

The Eu impurity bands are 3.7 eV above the top of the valence band and 0.41 eV for x=0.125, 0.14 eV for x=0.25 below the bottom of the conductive band (see the inset of Fig. 3a,b). This indicates the properties of electron trapping in which electrons need an activating energy of 3.7 eV to be trapped into Eu *f*-like band from the valence band and 0.41 eV for x=0.125, 0.14 eV for x=0.25 to escape from the impurity trap to the conduction band and to become the conducting electrons. The experimental observation of electron trapping properties of CaO:Eu (1 wt% and 5 wt%) was reported by V. G. Kravets [11] through the photoluminescence (PL) and stimulated photoluminescence (SPL) spectra. None of the following active bands 337, 365, 488 and 1064 nm (photon energies ε=3.67, 3.40, 2.54, 1.17 eV respectively) could give rise to the photoluminescence of CaO. Only with the deuterium lamp UV radiation (with maximum spectra distribution of radiation from 200 to 300 nm, 6.20>ε>4.10 eV), the stimulated photoluminescence could be detected. These photon energy data are in very good agreement with the band gap energy E_g=3.7 eV (activating energy for electron to be trapped) from our calculated band structure. Moreover, a stimulated photoluminescence of CaO:Eu can be achieved with IR stimulating radiation if the materials are pre-irradiated by the deuterium lamp UV radiation. The maximum of such SPL spectrum is shifted to the shorter wave length region (610nm) in comparison with the peak in the PL spectrum (640 nm) for the impurity concentration of 0.5 wt%. The corresponding shift of photon energy of ~0.10 eV is also in good agreement with the energy for trapped electrons to jump up to the conductive band from our *ab initio* calculations (0.41 eV for x=0.125 and 0.14 ev for x=0.25). For x=0.375, the electron trapping property disappeared because of the semiconductor-half metallic phase transition.

3.3 Magnetism in $Eu_{0.375}Ca_{0.625}O$

When the Eu concentration increased, the density of *f*-like states also increased so that the density of state (DOS) at the Fermi level becomes high enough for the exchange interaction to transfer some electrons from spin-down subband to spin-up subband. Therefore, an energy split between the two subbands appeared and the electronic property switched on the ferromagnetic order. Among doping concentrations under consideration, only x=0.375 satisfied the given condition. Hence, we observed a ferromagnetic band structure only for $Eu_{0.375}Ca_{0.625}O$ (Fig. 2d). The most obvious split was seen between the *f*-like subbands with a splitting gap E_s~4.4 eV which showed a strong ferromagnetism (see Fig. 4).

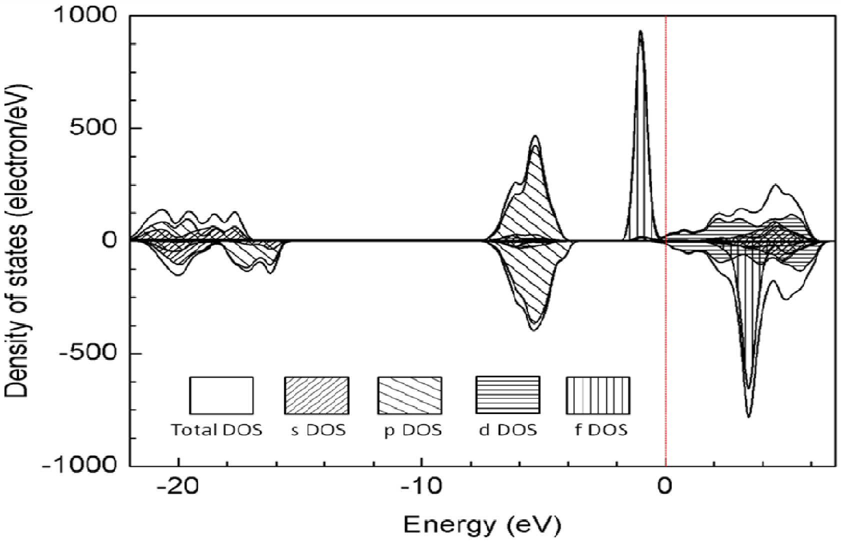


Fig. 4. Density of states of $Eu_{0.375}Ca_{0.625}O$ at ground state.

The paramagnetic state is $\Delta E=0.017$ eV above the ferromagnetic ground state. The Curier temperature of the material can be estimated by the mean field theory:

$$\Delta E=E_{kinetic}(T_C)=3/2k_BT_C \qquad (1)$$

where k_B is the Boltzmann constant, $E_{kinetic}(T_C)$ is the kinetic energy of an electron at $T=T_C$. We obtained $T_C=95K$. In the ferromagnetic state, the material is half metallic with metallic spin-up band and insulator spin-down band whereas the paramagnetic state is semiconductor with a small gap of 0.06 eV (see Fig. 5).

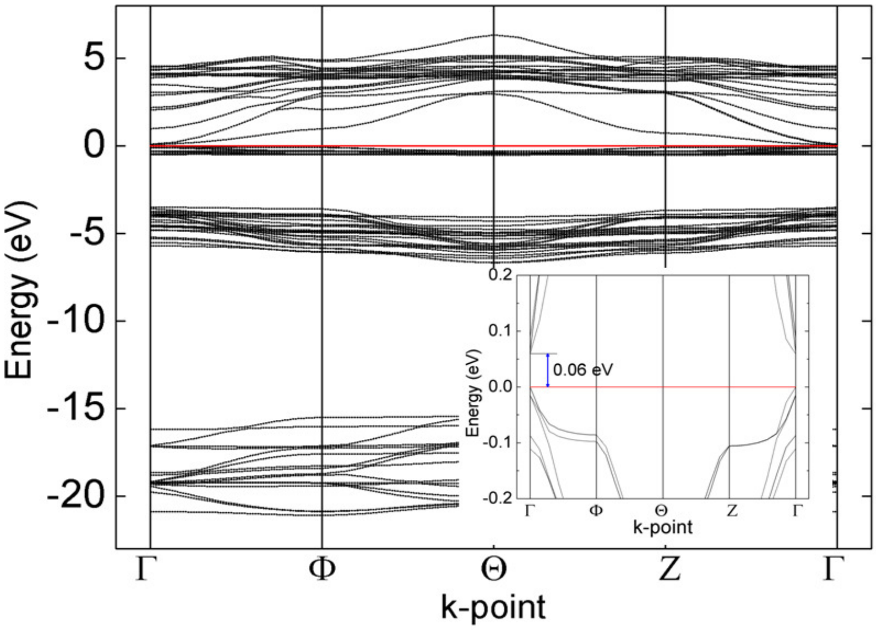


Fig. 5. Energy band structure of $Eu_{0.375}Ca_{0.625}O$ at paramagnetic state; the band gap is zoomed in in the inset.

4. Conclusion

In summary, although calcium oxide has been studied and used long time ago, our *ab initio* results argue for new applicability of this material in modern technology. The light doping of CaO with Eu could give rise to the electron trapping property which should disappear and the non-magnetic semiconductor - ferromagnetic half-metallic phase transition should occur simutaneously when the impurity concentration become large enough. So, both Eu light and heavy doped calcium oxides possess interesting properties which could make them suitable for application in modern spintronics. The obtained energy band structure parameters are also in very good agreement with experimental results, a part from the underestimated band gap value which could be explaned by the quantum confinement and occurence of F centers in the real materials.

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