



Electronic structure and magneto-optic Kerr effect in ferromagnetic titanium oxyphosphates $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$: An *ab-initio* study

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ABSTRACT

The X-ray diffraction for $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$, was used as a starting point to perform structural optimization by minimizing the forces acting on the atoms. We have performed a comprehensive theoretical study of electronic properties, including magneto-optic Kerr effect, of titanium oxyphosphates $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ in the ferromagnetic phase. The generalized gradient approximation (GGA) exchange-correlation potential was applied within the full potential linear augmented plane wave (FP-LAPW) method. The total energy of the ferromagnetic state is 0.72 eV less than that of the paramagnetic state. The total moment is found to be $2.99\mu_B$ with a major contribution of $2.47\mu_B$ coming from the Co atoms. In addition, we have calculated the total and partial densities of states. The electron charge densities and the bonding properties are analyzed and discussed. As a remarkable finding we note that the ferromagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$, is semiconducting with energy gap of about 1.2 eV for the minority spin and as semi-metallic for the majority spin, in contrast to the paramagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ which shows metallic behavior. From the calculated results of band structure and density of states, the half-metallic character and stability of ferromagnetic state for $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ is determined. The bonding properties of the ferromagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ have been analyzed through the electronic spin charge density contours in the (100) and (110) planes. The Kerr rotation spectrum is controlled by $\sigma_2^{xy}(\omega)$ at low energies (1.5–3.0 eV) because $\sigma_1^{xx}(\omega)$ is almost constant. The value of the Kerr rotation is close to 0.1 degree at low energies.

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1. Introduction

Extensive research work has recently been done to find semiconductors with improved ferromagnetic properties. The main thrust behind this research is to develop new spintronics devices like spin valves, spin light emitting diodes, magnetic sensors, logic devices and ultra-fast optical switches. These materials may be used as electro-optical devices and could be a good material for lithium batteries. For these reasons we have investigated the magneto-optic Kerr effect, and magnetic properties of spin-polarized ferromagnetic titanium oxyphosphates $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$.

Titanium oxyphosphates have been extensively studied for their structural, linear, nonlinear optical and electro-optical properties [1–7]. Belmal et al. [8] have studied the effect of substitution of a

monovalent ion by a divalent ion. They found that this substitution leads to a new series of titanium oxyphosphates. Belharouak and Amine [9] have studied $\text{Ni}_{0.5}\text{TiOPO}_4$ oxyphosphate in the (NiO–TiO₂–P₂O₅) ternary diagram as a novel insertion compound for lithium batteries. Carbon-coated $\text{Li}_{0.5}\text{Ni}_{0.25}\text{TiOPO}_4/\text{C}$ composite was synthesized [10] by the co-precipitation method using polyethylene glycol as carbon source. $\text{Li}_{0.5}\text{Ni}_{0.25}\text{TiOPO}_4/\text{C}$ composite exhibits excellent electrochemical performance with good capacity retention for 50 cycles. Approximately 200mAh/g could be reached at C, C/2, C/5 and C/20 rates in the 0.53 V potential ranges. It is clear that there is a dearth of theoretical work on titanium oxyphosphates $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$.

In our previous work [11] we studied the electronic properties of paramagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$. Our calculations showed that the paramagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ is metallic. Since Co is ferromagnetic it is natural to ascertain if this compound is paramagnetic or ferromagnetic. In the present work we have addressed ourselves to the study of the ferromagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$. Remarkably, we find that the ferromagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ is semiconducting with energy gap of about 1.2 eV for the minority spin and as semi-metallic for the majority spin.

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Theoretical studies are helpful in elucidating the relationship between structure and the dispersion of optical susceptibilities. In the past *ab-initio* density functional theory (DFT) calculations have been extensively applied for the computations of structural and optical parameters. Further, the efficiency of the optical susceptibilities is inherently dependent upon the structural features. As a result, it would be valuable to probe and understand the structural properties in this class of materials. A detailed description of the electronic properties, magneto-optic Kerr effect, and magnetic properties of spin-polarized ferromagnetic titanium oxyphosphates $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ using a DFT full potential method is very crucial and could give important insights into understanding the origin of the electronic properties, their relations with principal structural parameters, chemical bonds and their relation with magneto-optic Kerr effect. We would like to reiterate that one of the principal goals of the article is to establish the role of Co atoms in the modification of band energy structure and related electronic properties and to study the magneto-optical susceptibilities.

2. Structural features and computational details

The crystal structure of ferromagnetic titanium oxyphosphates $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ single crystals is shown in Fig. 1. The three dimensional structure of this material consists of corner sharing octahedral $[\text{LiO}_6]$, isolated $[\text{PO}_4]$ tetrahedral, and $[\text{TiO}_6]$ octahedral located between the titanium chains. The material also contains octahedral vacant sites that constitute favorable sites for lithium insertion. Asymmetric unit show that P is tetrahedrally coordinated by four O ions $[\text{PO}_4]$. The experiments [8] show that this compound has a crystal structure corresponding to monoclinic symmetry and space group $P21/c$. The experimental lattice parameters and the atomic position were given by Belmal et al. [8]. In the experimental paper it is mentioned that Co atoms have a fractional occupancy 0.5.

As the WIEN2K code does not handle fractional occupancies [11], we have chosen to do the calculations using a supercell corresponding to triclinic symmetry and space group $P-1$. In our previous work we had optimized the structure by minimization of the forces (1 mRy/au) acting on the atoms [11]. From the relaxed geometry the electronic structure and the chemical bonding can be determined and various spectroscopies can be simulated and compared with experimental data. Once the forces are minimized in this construction one can then find the self-consistent density at these positions by turning off the relaxations and driving the system to self-consistency.

We have employed full potential linear augmented plane wave (FP-LAPW) method based on spin-polarized density functional theory, as implemented in the WIEN2K package [12]. The generalized gradient approximation (GGA) exchange–correlation potential [13] was used. The core state electrons are treated relativistically and the scalar relativistic approximation is used for the valence states. We have performed a spin polarized calculation and have included spin–orbit (SO) coupling. Within a semi-relativistic approximation, self-consistent treatment of the valence states is performed, while the core states are treated self-consistently and fully relativistically relaxed in spherical approximation. The expansion of potential, charge density and basis functions is carried out within the radius of muffin-tin (MT) spheres along with spherical harmonic functions with a cut-off of $l_{\text{max}} = 10$ and with Fourier series in the interstitial region. The parameter $K_{\text{max}} = 9/R_{\text{MT}}$ is used for finding matrix size, where K_{max} is the plane wave cut-off and R_{MT} denotes the smallest of all atomic MT radii. The MT radii were assumed to be 1.87 atomic units (a.u.) for Li, 1.91 a.u. for Co, 1.7 a.u. for Ti, and 1.44 a.u. for O and P atoms. The self-consistency was achieved using 300 k -points

in the irreducible Brillouin zone (IBZ). The self-consistent calculations are converged since the total energy of the system is stable within 10^{-5} Ry.

From the total energy calculations, it is found that the total energy of the FM state is 0.72 eV per unit cell (which is composed of four formula units) lower than that of the paramagnetic state, indicating that the FM phase is more stable than the paramagnetic phase. The calculated total magnetic moment (M^{Tot}) is about $2.99\mu_{\text{B}}$. The magnetic moment (m) for Co is $2.47\mu_{\text{B}}$ and in the interstitial sites it is $0.17\mu_{\text{B}}$. The integer value of Bohr magneton of the magnetic moment is a typical character of half-metallic character (HM) ferromagnetism, which is consistent with the spin-dependent total DOS. Our calculations show that the major contribution to the magnetic moment comes from the Co atom with a small contribution from anion sites whose magnetic moments are parallel to the Co moments, and from the interstitial sites. Very small magnetic moments are induced from the spin delocalization of Co at Ti sites near the Co atoms when the Ti magnetic moments are parallel to the Co moments.

3. Results and discussion

3.1. Density of states and electron charge density distribution

The spin-polarized electronic band structure, total and partial densities of states up and down (DOS-up and DOS-dn) are presented in Fig. 2. The band structure and density of states show that $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ exhibits HM with the majority spin being semiconducting and the minority spin being semi-metallic. In the majority spin channel around the Fermi level there is an energy gap of about 1.2 eV, whereas the minority spin shows metallic nature. The valence band maximum (VBM) occurs at Γ -point of BZ and conduction band minimum (CBM) at C-point of BZ resulting in an indirect band gap. Comparing the total and partial density of states with the electronic band structure, we find that valence bands of the majority-spin electrons around the Fermi level generally comes from the Co-3d states with a small contribution of anion p states. The conduction band of the majority-spin electrons is totally dominated by Li-p, P-p and O-p states, while in case of the minority-spin the conduction band crosses the Fermi level, which leads to HM ferromagnetism. Our motivation was to see if this compound is ferromagnetic. Hence we used the same xc potentials as in the paramagnetic calculations that is LDA and GGA. Fig. 2 suggests that the band structure and DOS can be divided into six distinct spectral groups/structures. From the PDOS-up/dn we are able to identify the angular momentum character of the various structures. The lowest group (first group) which is located at -10.0 eV, the PDOS-up/dn is originating mainly from Li-p states with small contribution of Ti-s/p/f, P-s/p, Co-s/p and O-s states. The second group (-7.5 eV) the PDOS-up/dn arises from Ti-p with admixture of Ti-s/f, Li-s/p, P-s/p, Co-s/p and O-s/p states. The third group (-6.0 to -2.0 eV) the PDOS-up is a mixture of P-s/p, Ti-p/d/f, Co-s/p/d and O-s/p states, whereas in the PDOS-dn both of Ti-d and Co-d does not contribute. The fourth group from -2.0 eV up to Fermi energy, the PDOS-up show mixture of Co-d, O-s/p and Ti-p states, while PDOS-dn shifted toward $+2.0$ eV, and overlaps Fermi energy and shows mixture of Co-s/d, O-s/p and Ti-p states. The group from the conduction band maximum and above both of PDOS-up/dn is formed by Co-s/p/d, O-s/p, Li-s/p, Ti-s/p/d/f and P-s/p states. Following Fig. 2, we note that in both PDOS-up/dn there is a strong hybridization between Li-s and Co-s/p states, Ti-p with O-s, Ti-d with Co-d and Li-p with Ti-s, P-s/p states.

We find that ferromagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ is half-metallic. It shows a semiconductor behavior with energy band gap of about 1.2 eV for spin up and a semi-metallic behavior for spin down with

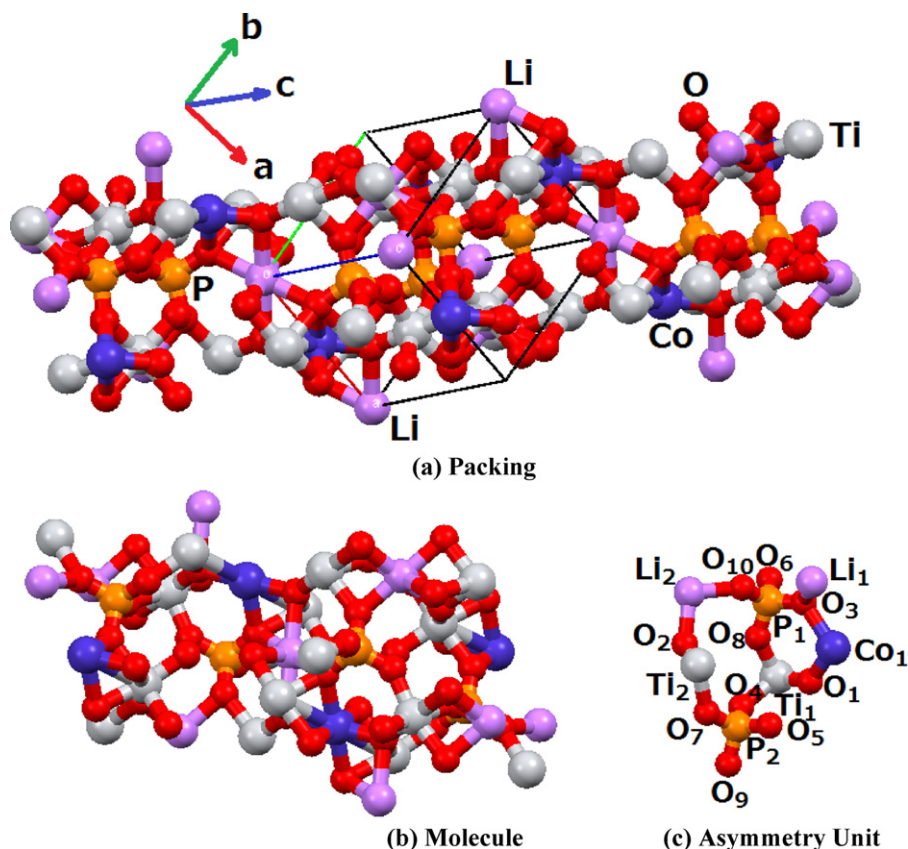


Fig. 1. Crystal structure of the ferromagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$.

a DOS at E_F , $N(E_F)$ of about 0.59 states/Ry cell and the bare electronic specific heat coefficient (γ) 0.102 mJ/mol K^2 for GGA. In comparison to the paramagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$, which is found to be metallic with a $N(E_F)$ of about 3.0 (2.66) states/Ry cell using GGA (EVGGA), and γ is 0.52 (0.46) mJ/mol K^2 for GGA (EVGGA) (our previous work [11]).

From analysis of the partial density of states we find some electrons from Co-d, Li-p, P-p, Ti-p and O-p states (CBs) are transferred into valence bands (VBs). This leads to weak covalence interactions between O–O, Ti–Ti, Li–Li, P–P and Co–Co pairs, and stronger between Co–O, Co–Ti, and Ti–O pairs. Thus the covalent strength between dissimilar atoms is stronger than between similar atoms.

We have plotted the electronic spin charge density contour in the (110) -up/dn and (100) -up/dn planes as shown in Fig. 3a–d. The contour plot shows more ionic and partial covalent bonding between Li–O which depends on Pauling electro-negativity difference of Li (0.93) and O (3.58) atoms. As a result, we observe a large Li electronic charge transferred to O site. This can be seen easily by color charge density scale where blue color (+1.000) corresponds to the maximum charge accumulation site. The interaction between Co–O produces covalent-like bond due to small electro-negativity difference around 0.7 (electro-negativity of Co is 1.88) and also due to the hybridized Co-3d states with O-p states. The localized Co-3d states produce more ionic nature between Co–O bonds. In spin-up, Co charge affects the bonding more than in the spin-down state. Also the electronic charge density between Ti(1.54)–O, shows more strong covalent bonding. In Tables 1 and 2 we have listed the bond lengths and angles for some selected atoms for the ferromagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ in comparison with the experimental data [8] and the theoretical results of the paramagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ [11]. Following Table 1 we notice that the largest bond length of Co–O in ferromagnetic

$\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ is 2.200 Å which is larger than the bond length of Co–O in pure CoO in the rocksalt structure (2.130 Å) and the experimental value (2.140 Å) [8] and theoretical value (1.924 Å) [11] of Co–O of the paramagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$. That would suggest higher magnetic moments. This could here occur because of the open corner sharing octahedral structure and the fact that some O belong to the PO_4 tetrahedra. From Table 2 one could notice that in the ferromagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ the O5 and O2 atoms exchange their positions and hence the bond angles of O3–Ti2–O5 and O2–Ti2–O3 in comparison with the experimental data [8] and the theoretical results [11]. We should emphasize that the Ti–O complex crystals may be also very promising for nonlinear optics as a result of different cationic substitution. Additionally the large

Table 1
Bond lengths (Å) of selected $[\text{PO}_4]$ tetrahedral.

Bond lengths	Ferro*	Exp.	Para**
P2–O4	1.538	1.56(3)	1.55
P2–O5	1.547	1.57(2)	1.56
P1–O3	1.580	1.56(2)	1.55
Li1–O1	2.262	2.11(1)	2.10
Li2–O2	2.076	2.25(2)	2.23
Co1–O1	1.924	2.14(2)	2.15
Co1–O1'	1.924	2.14(2)	2.15
Co1–O7	2.001		
Co1–O3	2.200		
Ti1–O1	1.805	1.68(2)	1.66
Ti1–O2	2.133	2.03(3)	2.03
Ti1–O4	2.044	1.99(1)	2.00
Ti2–O5	1.917	1.86(2)	1.85

* This work ferromagnetic.

** Previous work paramagnetic [11].

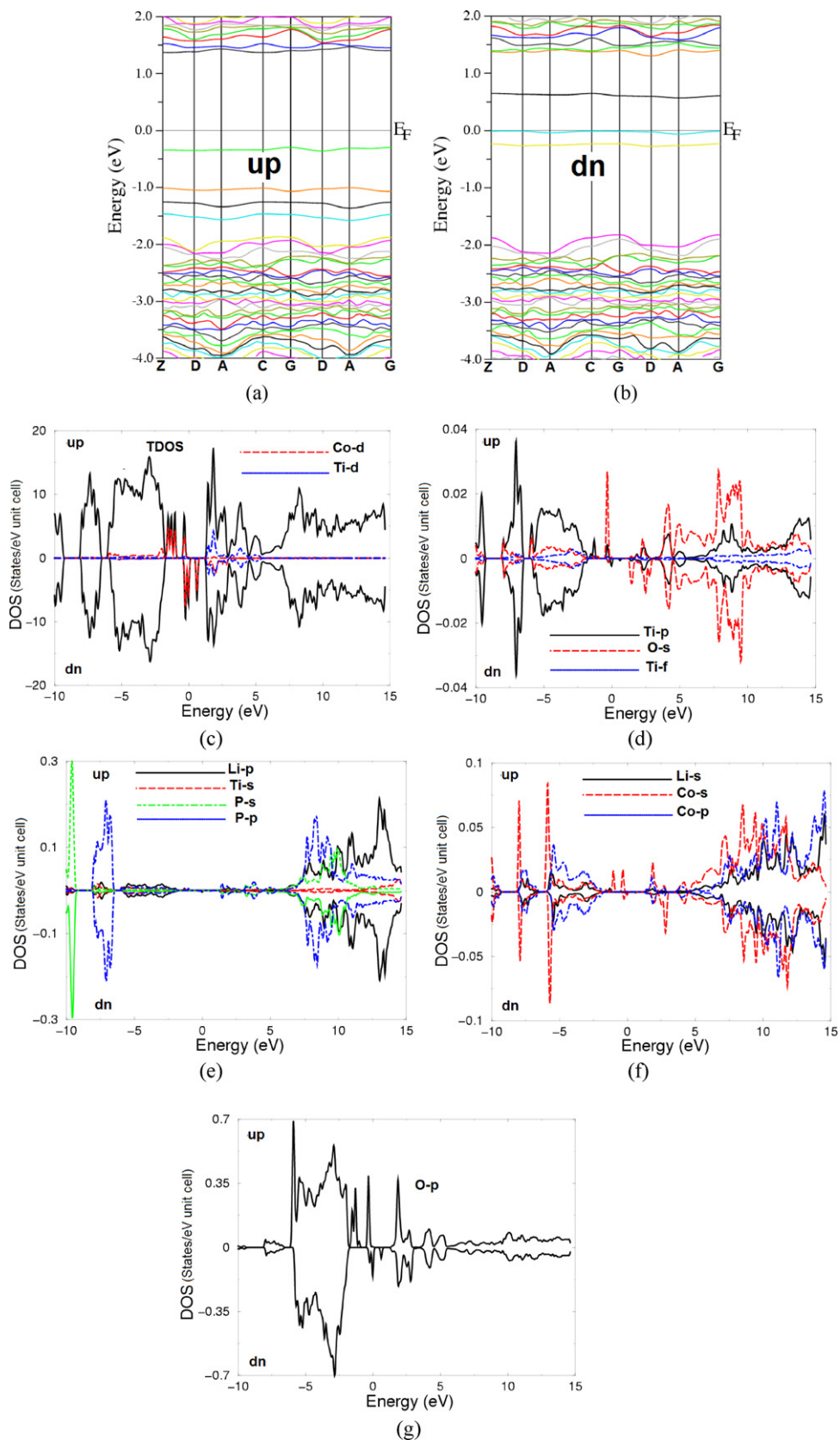


Fig. 2. (a–b) Calculated spin-polarized band structure, the colors are used just to distinguish between the bands; (c–g) calculated spin-polarized total and partial density of states (states/eV unit cell) of the ferromagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$.

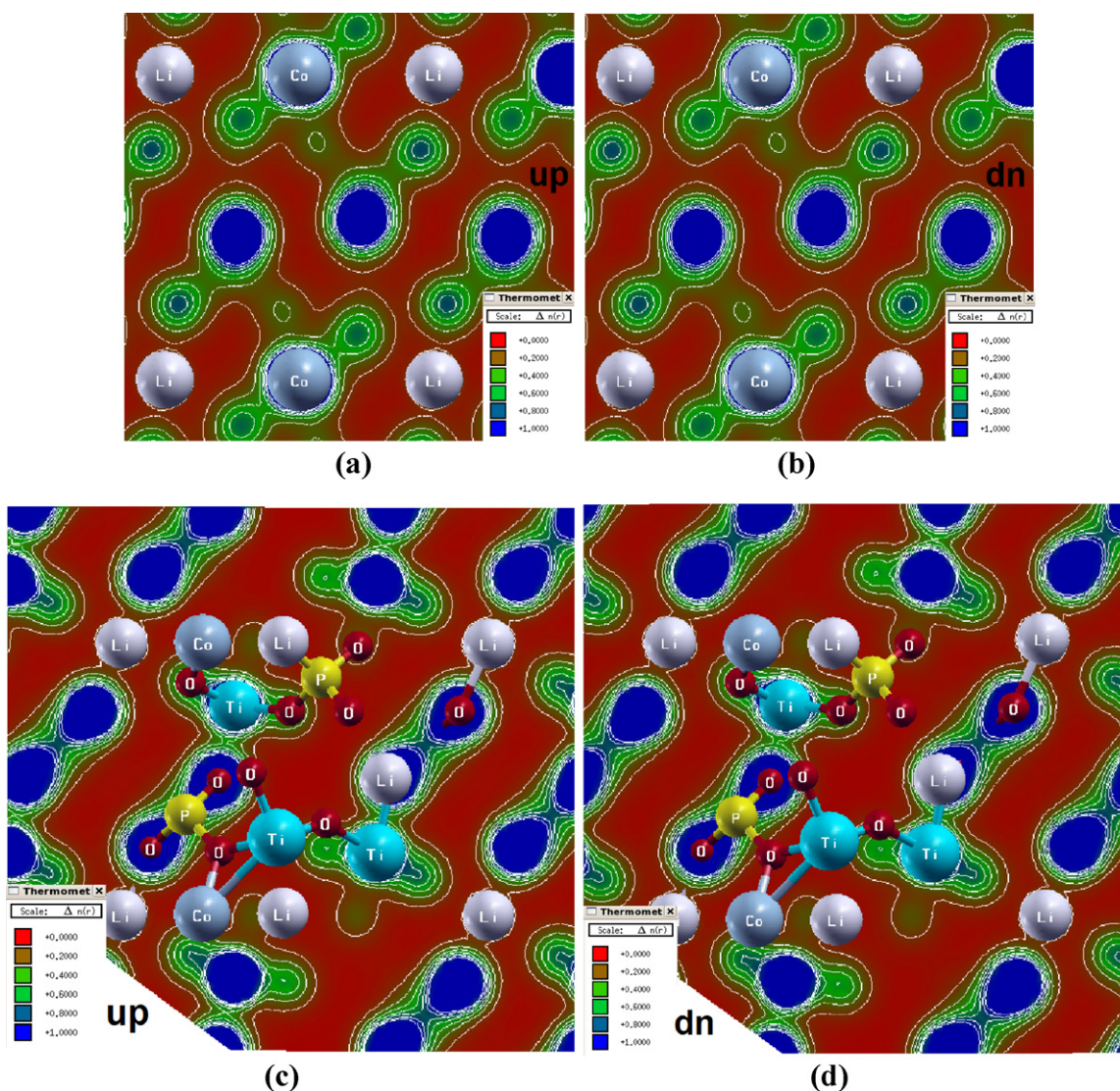


Fig. 3. Calculated spin-polarized electronic charge density contours: (a, b) in the (100) up/dn and (c, d) in the (110) up/dn planes of the ferromagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$.

part of ionic chemical bonds may favor enhanced electron–phonon interactions.

3.2. Magneto-optical properties

The calculation of magneto-optical properties requires an accurate description of the Kohn–Sham eigenvalues and eigenvectors, which motivates the use of a full potential method. Since the magneto-optical properties arise from the exchange splitting in

combination with spin-orbit coupling, their result suggests that the full potential treatment will be important in order to describe the magneto-optical properties properly. The plane polarized light become elliptically polarized when it reflect or transmit through materials with nonzero magnetization. The effect due to reflection is called magneto-optical Kerr effect, while due to transmission is the magneto-optical Faraday effect [14,15]. The magneto-optical Kerr effect and magneto-optical Faraday effect are zero in the absence of spin-orbit interaction or if there is no spin polarization. It is a consequence of the removal of time reversal symmetry for the entire system and is therefore a particularly sensitive test of relativistic energy band theory. Fig. 4a shows the Kerr rotation which is representative of the real part of Kerr effect while Fig. 4b illustrated the Kerr ellipticity (imaginary part of Kerr effect). We would like to mention that we not aware of any experimental data or theoretical results of the Kerr effect for the investigated compound. The form of the optical conductivity tensor is written as:

$$\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ -\sigma_{xy} & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$$

We must note that this is valid for cubic systems when the magnetic field is along the z-axis. Although we have a monoclinic

Table 2
Bond angles ($^\circ$) of selected $[\text{PO}_4]$ tetrahedral.

Bond angles	Ferro*	Exp.	Para**
O1–Li1–O1'	180.00	180.0(1)	179.3
O1–Ti2–O3	168.34	169.6(4)	160.0
O2–Ti1–O4	79.90	80.8(1)	81.0
O1–Ti1–O2	78.24	98.5(1)	98.0
O1–Ti2–O5	90.20	99.5(1)	100.0
O3–Ti2–O5	162.05	93.1(2)	92.8
O2–Ti2–O3	96.48	160.6(4)	160.0
O2–Ti2–O5	91.39	89.3(3)	90.0

* This work ferromagnetic.

** Previous work paramagnetic [11].

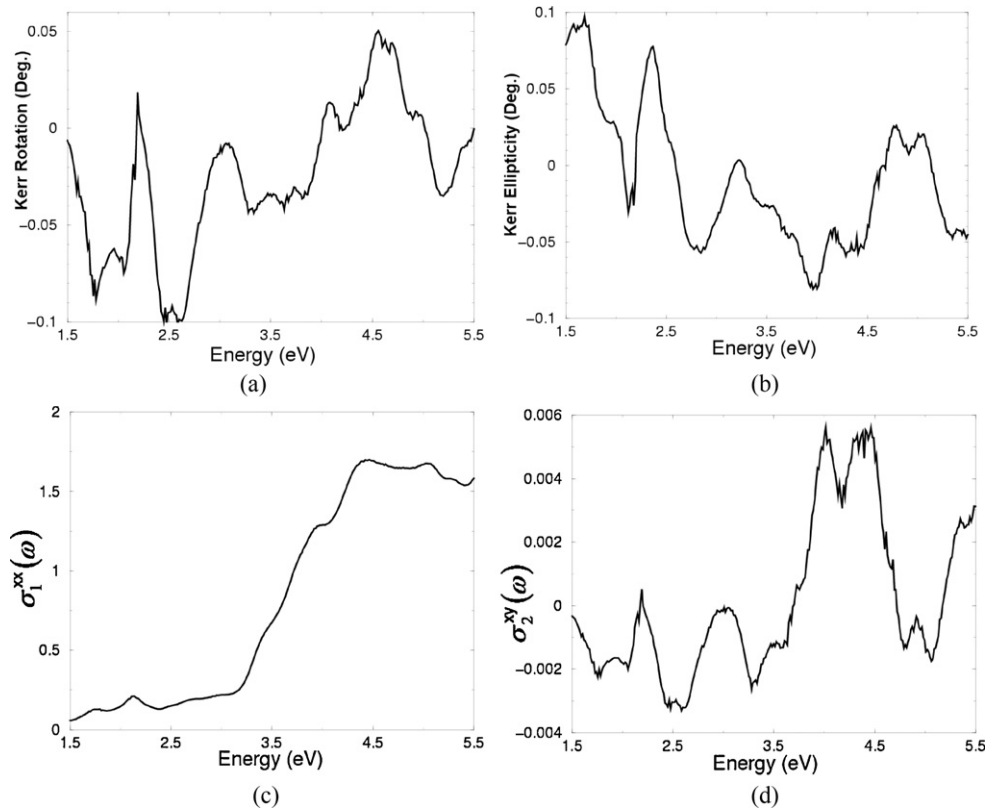


Fig. 4. (a) Calculated Kerr rotation; (b) calculated Kerr ellipticity; (c) calculated $\sigma_1^{xx}(\omega)$; (d) calculated $\sigma_2^{xy}(\omega)$.

structure for the supercell, we have still used this tensor. This is an approximation in our MOKE calculations. A look at the crystal structure shows that two of the lattice constants are almost equal and one is 10% smaller and two angles are right angles and one is 90.36. Thus to a reasonable approximation the formula for cubic structure may not be a very bad approximation.

The interband contribution to the absorptive part of the optical conductivity $\sigma_2^{xy}(\omega)$ was calculated by summing up the transitions from occupied to unoccupied states giving by [16]

$$\sigma_2^{xy}(\omega) = \frac{Ve^2}{8\pi^2\hbar m^2\omega} \sum_{nn'} \int d^3k \langle kn | p_x | kn' \rangle \langle kn' | p_y | kn \rangle f_{kn}(1 - f_{kn'}) \delta(\varepsilon_{kn'} - \varepsilon_{kn} - \hbar\omega)$$

where $p = -i\hbar\nabla$ is the momentum operator, f_{kn} is Fermi distribution function, and $|kn\rangle$ the crystal wave function corresponding to eigenvalue ε_{kn} with crystal momentum k , and $\delta(\varepsilon_{kn'} - \varepsilon_{kn} - \hbar\omega)$ is the condition for total energy conservation.

Fig. 4c shows real part of conductivity $\sigma_1^{xx}(\omega)$, and the absorptive part $\sigma_2^{xy}(\omega)$ of the off-diagonal conductivity is presented in Fig. 4d. We note that $\sigma_1^{xx}(\omega)$ in the visible range 1.5–3.0 eV is almost constant with no structure. Hence the structure in Kerr spectrum is governed by the structure in $\sigma_2^{xy}(\omega)$. The Kerr angle for the visible part of the spectrum is small and around 0.1° .

4. Conclusion

We find that the ferromagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ is a semiconductor with energy gap of about 1.2 eV for the minority spin and semi-metallic for the majority spin with a DOS at E_F , $N(E_F)$ of about 0.59 states/Ry cell and the bare electronic specific heat coefficient 0.102 mJ/molK^2 for GGA. In comparison

to the paramagnetic $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$, which is found to be metallic with a $N(E_F)$ of about 3.0 (2.66) states/Ry cell using GGA (EVGGA). We should emphasize that this material could be useful for spintronics application, because it exhibits semiconductor nature for the minority spin ($P=1$). From the total energy calculations, we find that the energy of the FM state is lower than the paramagnetic state, indicating that the FM phase is more stable than the paramagnetic phase for the experimental lattice constant. The calculated total magnetic moment is about $3.00\mu_B$. The magnetic moment for Co is $2.47\mu_B$ and in the interstitial sites it is $0.17\mu_B$. We have performed a comprehensive theoretical study of electronic properties, magneto-optic Kerr effect and magnetic properties of spin-polarized ferromagnetic titanium oxyphosphates $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$. The generalized gradient approximation exchange-correlation potential was applied within the full potential linear augmented plane wave method. In addition we have calculated the spin-polarized total and partial densities of states. The electron charge densities and the bonding properties were analyzed and discussed. The electronic charge density contour in the (100) and (110) crystallographic plane was calculated to explain the bonding properties. The contour plot shows more ionic and partial covalent bonding between Li–O, and large Li electronic charge transferred to O site. The interaction between Co–O produces covalent-like bond and the localized Co-3d states produce more ionic nature between Co–O bonds.

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