M. Ibrir[1], S. Lakel[2] and Saadi Berri[3]

Electronic structure and magnetic properties of KXF₃(X= Fe, Co, Mn, V) from ab initio calculations.

M. Ibrir[1], S. Lakel[2] and Saadi Berri[3]

[1]Laboratory of Physics of Materials and its Applications
Department of Physics
University Med BOUDIAF Msila
B. P. 166, 28000 MSila, Algeria.

[2]Laboratory of Metallic and Semiconducting Materials
Department of Physics
University of Biskra
B.P. 145, RP 07000 Biskra, Algeria.

[3]Laboratory for Developing New Materials and their Characterizations,
Department of Physics
University of Setif, Algeria.

Abstract

In this work we have performed first-principle calculations of the structural, electronic and magnetic properties of $KFeF_3$, $KCoF_3$, $KMnF_3$, KVF_3, using full-potential linearized augmented plane-wave (FP-LAPW) scheme within GGA. Features such as the lattice constant, bulk modulus and its pressure derivative are reported. Also, we have presented our results of the band structure and the density of states. The magnetic moments of $KFeF_3$, $KCoF_3$, $KMnF_3$, KVF_3 compounds are in most came from the exchange-splitting of X-3d orbital.

Keywords: Magnetic materials; Ab initio calculations; Electronic structure.

[*] Corresponding author : E-mail : ibrirmiloud@yahoo.fr

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1. Introduction

The cubic perovskites with varied compositions and structures have been extensively studied, motivated by their possible applications in numerous industrial and engineering domains [1-5]. They have showed a wide range of attractive properties ferroelectricity [6–8], piezoelectricity [9,10], semiconductivity [11], catalytic activity [12], thermoelectricity [13], superconductivity and metal-insulator transition [14]. As an example ternary oxides of rare earth (Eu, Gd, Tb)CoO_3 type oxides, this series reveal extensive applications in materials science and technology, some of the perovskites (Eu, Gd, Tb)CoO_3 compounds are used as electrode materials for magnetohydrodynamic (MHD) generators[15], for fuel cells [16]. On the other hand, perovskites like $BaMnO_3$ and $SrMnO_3$ have attracted interest in NO removal process as catalysts [17–19].

Recently, half-metallic ferromagnetism has been found in CrO_2 [20], NiMnSb [21], Fe_3O_4 [22], $La_{0.67}Sr_{0.33}MnO_3$ [23], Co_2MnSi [24], Ti_2FeSi [25], Ti_2CoAl [26], NiCr(P, Se, Te, As) [27], Pb_2FeMoO_6[28], and CoFeMnZ (Z = Al, Ga, Si, Ge) [29], and nearly 100% high spin-polarization has been observed experimentally in the cases of CrO_2 and $La_{0.67}Sr_{0.33}MnO_3$ materials [30]. Half-metallic ferromagnets (HMF) meet all the requirements of spintronics, as a result of their exceptional electronic structure. These materials behave like metals with respect to the electrons of one spin direction and like semiconductors with respect to the electrons of the other spin direction.

Generally, KXF_3 compounds crystallize in the cubic symmetry (space group *Pm3m*). In this structure, X atom occupy (1/2;1/2;1/2) position, K atom at (0;0;0) and F atom at (1/2;1/2;0). In the present paper, the structural, electronic and magnetic properties of KXF_3 compounds are reported.

Our main goal in this work is to evaluate examine the validity of the predictions of half metallicity for KXF_3 compound, The calculations are performed using ab initio full-potential linearized augmented plane wave (FP-LAPW) scheme within GGA approach. Our paper is organized as follows. The theoretical background is presented in Section 2. Results and discussion are presented in Section 3. A summary of the results is given in Section 4.

2. Method of calculations

We have carried out first-principles calculations [31, 32] with both full potential and linear augmented plane wave (FP-LAPW) method [33] as implemented in the WIEN2k code [34] within the density functional theory (DFT). The Perdew–Burke–Ernzerhof generalized gradient approximation GGA [35, 36]. In the calculations reported here, we use a parameter $R_{MT}K_{max}$=9, which determines matrix size (convergence), where K_{max} is the plane wave cut-off and R_{mt} is the smallest of all atomic sphere radii. We have chosen the muffin-tin radii (MT) for to 2.05, 2.0, 1.95, 1.8 and 1.3 (a.u) for Co,

Fe, Mn, K and F atoms respectively. Within the sespheres, thecharge density and potential are expanded in terms of crystal harmonics up to angular momenta $L=10$, and a plane wave expansion has been used in the interstitial region. The value of $G_{max}=14$, where G_{max} is defined as the magnitude of largest vector in charge density Fourier expansion. The Monkorst-Pack special k-points were performed using 3000 special k-points in the Brillouin zone. The cut off energy, which defines the separation of valence and core states, was chosen as -6 Ry. We select the charge convergence as $0.0001e$ during self-consistency cycles.

3. Results and discussion

We have calculated the total energy as a function of lattice constant of KXF_3 compound for the ferromagnetic (FM) state. The plots of calculated total energies versus reduced volume of KXF_3 compounds is given in Fig.1. The total energies versus changed volumes are fitted to the Murnaghan's equation of state [37] in order to determine the ground state properties, such as equilibrium lattice constant a, bulk modulus B and its pressure derivative B'. The calculated structural parameters of KXF_3 compound is reported in Table 1.

Our results for the lattice parameters of KXF_3 compounds are in good agreement with previous theoretical and experimental data [38-44]. The lattices parameters of $KFeF_3$, $KCoF_3$, $KMnF_3$ and KVF_3 compounds increases in the following sequence: $a(KMnF_3) < a(KVF_3) < a(KFeF_3) < a(KCoF_3)$. Furthermore, atomic radii of X elements do not increase, as the authors state, but rather decrease in the following sequence: R(Mn= 0.83Å)> R(V= 0.79Å)> R(Fe= 0.78Å)> R (Co=0.745Å) [42]. On the other hand, the calculated B values decreases in the following sequence: $B(KCoF_3) > B(KFeF_3) > B(KVF_3) > B(KMnF_3)$. The calculated bulk modulus B and its pressure derivative B' of the KXF_3 compounds are reported in the Table 1, together with theoretical data [38] for the sake of comparison.

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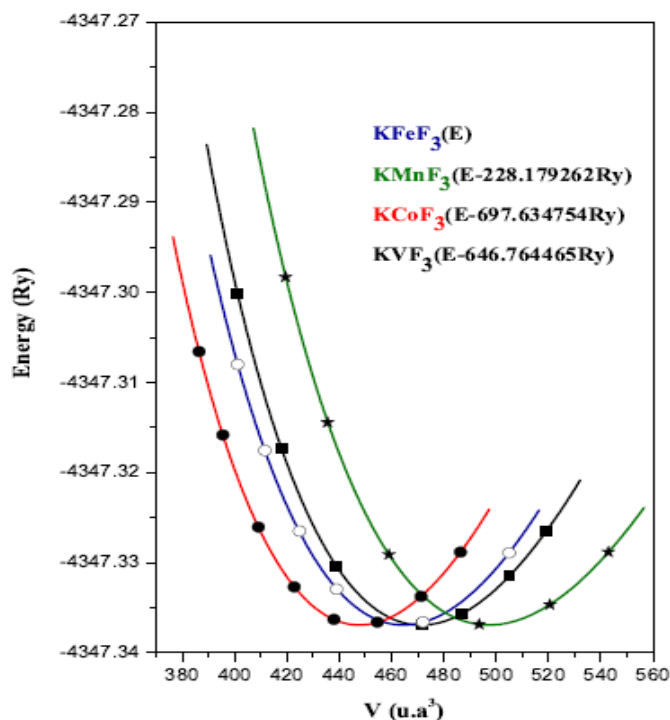
Fig. 1. The volume optimization for KVF_3 (Black curve), $KCoF_3$ (Red curve), $KFeF_3$ (Blue curve) and $KMnF_3$ (green curve).

Table.1 Calculated a (in Å), B (in GPa) and its pressure derivative B' for $KXF3$($X=$ Fe, Co, Mn and V), together with experimental and theoretical data for comparison purpose.

		a	B	B'
$KFeF_3$	Present work	4.098	76.879	3.925
	Theory	4.138 [40]	-	-
		4.138 [41]	-	-
		3.837 [42]	-	-
		4.22 [38]	69 [38]	-
		4.12 [39]	-	-
	Exp	4.138 [40]	-	-
$KCoF_3$	Present work	4.048	81.905	4.187
	Theory	4.077 [40]	-	-
		4.072 [41]	-	-
		3.801 [42]	-	-
		4.16 [38]	74 [38]	-
		4.06 [39]	-	-
	Exp	4.071 [40]	-	-
$KMnF_3$	Present work	4.192	66.840	4.867
	Theory	4.185 [40]	-	-
		4.184 [41]	-	-
		3.889 [42]	-	-
		4.28 [38]	65 [38]	-
		4.19 [39]	-	-
	Exp	4.189 [40]	-	-
KVF_3	Present work	4.118	75.184	4.686
	Theory	4.134 [40]	-	-
		4.134 [41]	-	-
		3.847 [42]	-	-

Exp		4.1	[40]	-	-

The calculated spin-polarized band structures of KXF_3 compounds at the theoretical equilibrium lattice constant along high-symmetry directions of the first Brillouin zone are displayed in Fig. 2. The total and partial densities of states, in which the spin-up and spin-down sub-bands are plotted with black and red lines, respectively, are shown in Fig. 3. The Fermi level set as 0 eV. Note that for KVF_3 and $KMnF_3$ compounds, the valence band maximum (VBM) is located at point *R*, whereas the conduction band minimum (CBM) is located at *Γ* point (see Fig. 2.(a, b)), leads to a gap of about 6.41eV and 6.18eV for KVF_3 and $KMnF_3$ respectively. These compounds behave as semiconductor for spin-up polarization and as isolator for spin-down polarization. On the other hand, 100% spin polarized at the Fermi level which indicates that KVF_3 and $KMnF_3$ compounds have half metallic behavior. In the case of $KCoF_3$ and $KFeF_3$ compounds (see Fig. 2.(c, d)), in the minority spin part, local and mostly no hybridized (Co, Fe)-dt2g states are found at about ≈0.4 eV above the Fermi leve, confirm the metallic behavior for spin-down polarization, and a gap opens in the majority spin band, these compounds behave as semiconductor for spin-up polarization.
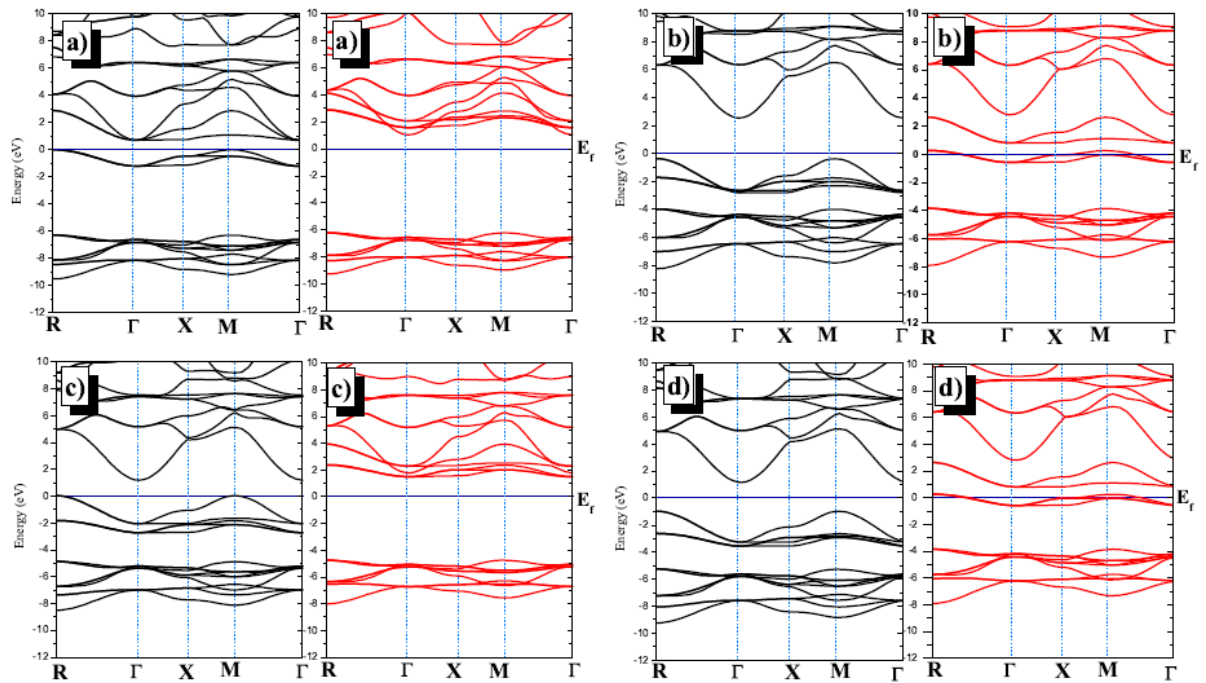

Fig. 2. The up-and down-spin band structures of a) KVF_3, b) $KMnF_3$, c) $KCoF_3$ and d) $KFeF_3$ compounds.

In Fig. 3 shows the total density of states and partial density of as a function of energy for the KXF_3 compounds at its equilibrium lattice constant. To illustrate the nature of the electronic band structures, we have plotted the partial density of states (DOS) of K-d, X-(d-eg and d-t2g), and F-p electrons for the spin-up and spin-down sub-bands, the figure indicates that band structures can be divided into three parte: at the energie rigon from:(1) –12.0 to –4.0 eV we find the contribution of F-p states, (2) -4.0 to 3.0 eV, which reprsents   the contribution of X-(d-eg and d-t2g) orbital, (the exchange-splitting between the spin-up and spin-down sub-bands of the X-(d-eg and d-t2g) states,

which are the main contributor in the magnetic moment), and (3) 3.0 to 10.0 eV is from the contribution of K-d states.

The calculated total m and atom-resolved magnetic moments for the KXF3 compounds are summarized in Table 2. The present study shows that the total magnetic moment is ≈4.96, ≈3.98, ≈2.99 and ≈ 2.96 μ_β for KMnF3, KFeF3, KVF3 and KCoF3 compounds respectively. Our results for the magnetic moments of KXF3 compounds are in good agreement with previous theoretical and experimental data [38, 43, 44]. For KXF3 compound, the effective magnetic moments are originated from the exchange-splitting of 3d state of X atoms.
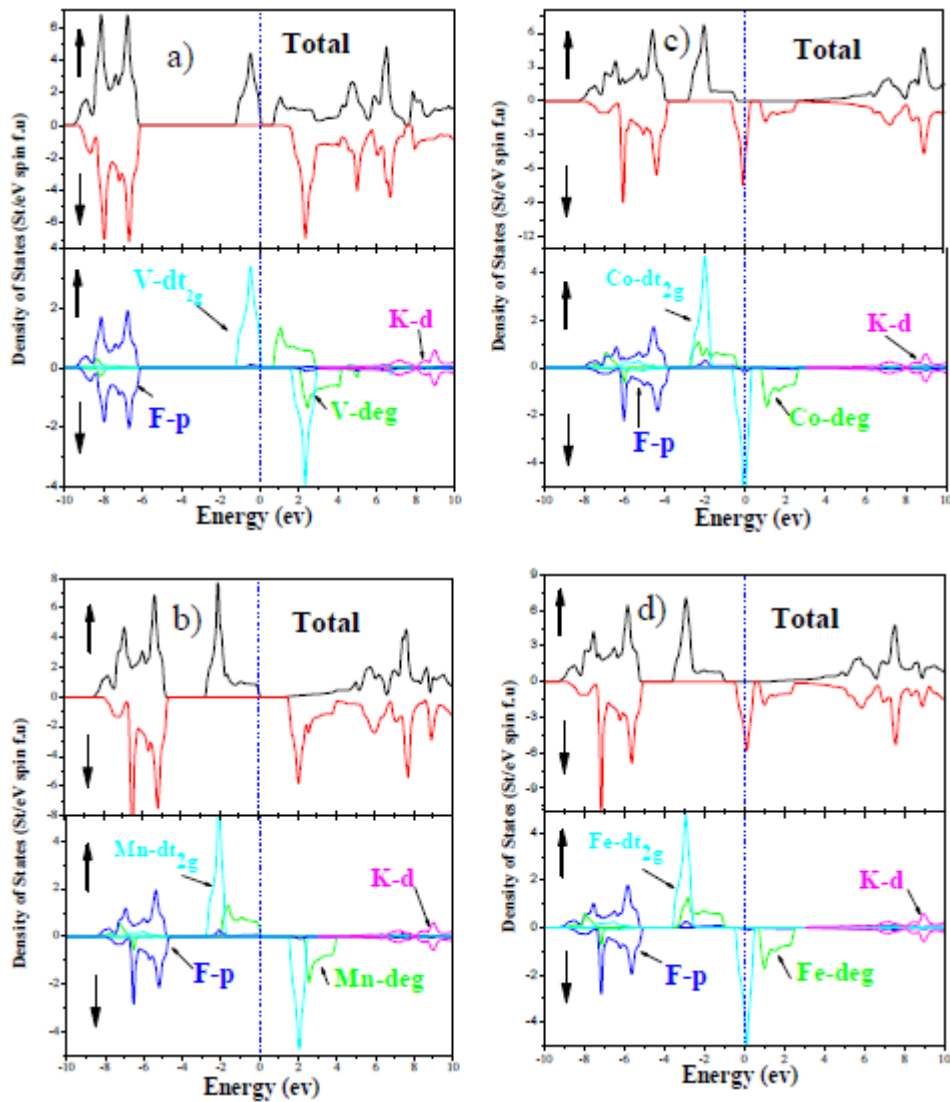
Fig. 3. Spin polarized total and partial density of states (DOS) of: a) KVF₃, b) KMnF₃,
c) KCoF₃ and d) KFeF₃ compounds.

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Table. 2. The calculated total and partial magnetic moment (in μ_B) for KXF3(X= Fe, Co, Mn and V) compounds.

Compound		interstitial region	K	F	X	Total magnetic moment
KFeF$_3$	GGA	0.18033	-0.00108	0.08438	3.55589	3.98889
	Exp	-	-	-	-	4.27 [43]
		-	-	-	-	4.49 [44]
	Other[38]	-	-	-	3.43	-
KCoF$_3$	GGA	0.04202	-0.00231	0.08682	2.66181	2.96199
	Exp	-	-	-	-	3.92 [43]
	Other[38]	-	-	-	2.3	-
		-	-	-	-	4.12 [44]
KMnF$_3$	GGA	0.44260	-0.00109	0.06887	4.31422	4.96232
	Exp	-	-	-	-	4.86 [43]
		-	-	-	-	4.93 [44]
	Other[38]	-	-	-	4.33	-
KVF$_3$	GGA	0.55177	0.00261	0.02384	2.36717	2.99398

4. Conclusion

For the KXF$_3$ compound, the electronic structure and magnetic properties have been calculated using the first principles full-potential linearized augmented plane waves (FPLAPW) method. The calculated lattice constants are in good agreement with experimental data. The insulating behavior of KMnF$_3$ and KVF$_3$ is brought out successfully by the present calculations. However, the above expected feature is absent in the KFeF$_3$ and KCoF$_3$ compounds. For KXF$_3$ compounds, the exchange splitting of X-3d electrons are responsible for ground state ferromagnetism.

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