Spinelectronic investigation of the quaternary vanadium fluoride Rb₂NaVF₆: Ab-initio method

M. Berber[a,b,*], B. Nour Bouzouira[a,c], H. Abid[d], A. Boudali[e], and H. Moujri[f]

ᵃCentre Universitaire Nour Bachir El Bayadh, 32000 El Bayadh, Algérie,
ᵇLaboratoire d'Instrumentation et Matériaux Avancés,
Centre Universitaire Nour Bachir, El-Bayadh, BP 900 route Aflou, 32000, Algérie,
ᶜLaboratory of Physical Chemistry of Advanced Materials, University of Djillali Liabes,
BP 89, Sidi-Bel-Abbes 22000, Algeria.
ᵈApplied Materials Laboratory, Research Center,
Sidi Bel Abbés Djillali Liabes University, 22000, Algeria.
ᵉLaboratory of Physico-Chemical Studies, University of Saida, 20000 Saida, Algeria.
ᶠRenewable Energy Laboratory and dynamic systems,
Faculté des Sciences Ain-Chock, Université Hassan II de Casablanca, Morocco.

In this study, we have investigated the structural, electronic, and magnetic properties of the Rb₂NaVF₆ compound. We have performed our calculations by the use of first-principle methods based on spin-polarized density functional theory, where the electronic exchange-correlation potential is treated by the generalized gradient approximation GGA- PBEsol coupled with the improved TB-mBJ approach. The calculated structural parameters of Rb₂NaVF₆ are in good agreement with the available experimental data. Rb₂NaVF₆ exhibits a half-metallic ferromagnetic feature with a spin polarization of 100% at the Fermi level and a direct large half-metallic gap of 3.582 eV. The total magnetic moments are 2 μB. This material is half-metallic ferromagnets, and it can be potential candidates for spintronics applications at a higher temperature.

1. Introduction

Spintronics is the investigation of the fundamental spin of the electron and its combined magnetic moment, adding to its essential electronic charge, in solid-state devices [1]. Furthermore, to charge state, electron spins are used as a further degree of freedom, with employment in the performance of data storage and transfer. Spintronic devices are almost frequently synthesized in dilute magnetic semiconductors (DMS), Perovskite, and Heusler alloys and are of exceptional attraction in the field of quantum computing and neuromorphic computing [2]. Spintronics is a field of study in which, researchers are looking for materials to ameliorate the accomplishment of their electronic and magnetic properties and get a large half-ferromagnetic (HM) gap (G_{HM}). The HM *i.e.*, spin-flip excitation, gap is identified to be the least possible energy with respect to the Fermi level of the majority (minority) spin between the minimal energy of the conduction bands and the absolute value of maximum energy of the valence bands [3,4]. Last decade, several experimental and theoretical research have been developed for this purpose. Recently, multiple works have treated the magnetic properties of the binary semiconductor III-V and II-VI doped by transition elements, Mn-doped InSb [5], Cr doped InSb [6], V doped GaP [7], Co-doped ZnS and (Al, Co) co-doped [8], and Mn-doped ZnO [9]. Shabir *et al.* studied the double perovskites system Ba₂CoUO₆ and report half-metallic comportment, with

a half-metallic gap $G_{HM} = 1.98$ eV [10]. A. Rafi *et al.* studied the perovskite selenide and tellurite compounds CoSeO₃, CoTeO₃, NiSeO₃, and NiTeO₃ [11]. The half-Heusler Alloy MgCaB has been investigated by A. Abada [12], with a value of G_{HM} of about 0.305 eV.

This aim of this work is to predict the structural, electronic, and half-metallic ferromagnetic properties of quaternary vanadium fluoride Rb₂NaVF₆. We have used in our calculation the generalized gradient approximation functional (GGA-PBEsol) [13] and Becke-Johnson exchange potential [14] with Tran-Blaha modified Becke-Johnson (TB-mBJ) potential [15] based on full-potential linearized augmented plane-wave (FP-LAPW) method within first-principle approaches of spin-polarized density functional theory (SP-DFT) [16]. This article is redacted as follows: In Sec. 2, we describe the method of the calculation. In Sec. 3, we demonstrate the details of the collected results and discuss the structural, electronic, and magnetic properties of the Rb₂NaVF₆ compound. Section 4 summarizes the key findings of our current research.

2. Computational method

In this study, we have utilized the FP-LAPW method based on SP-DFT [16] as realized in the WIEN2K software [17,18] to predict the structural, electronic, and magnetic properties
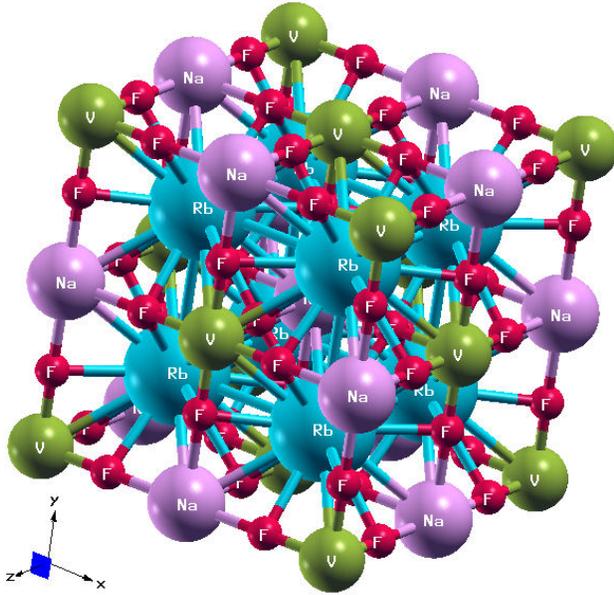
FIGURE 1. Crystal structure of quaternary vanadium fluoride Rb$_2$NaVF$_6$.

TABLE I. Rb, Na, V and F atoms positions.

Atoms		Position		
		X	Y	Z
Rb	Atom 1	0.250	0.250	0.250
	Atom 2	0.750	0.750	0.750
Na	Atom 1	0.500	0.500	0.500
V	Atom 1	0.000	0.000	0.000
F	Atom 1	0.230	0.000	0.000
	Atom 2	0.770	0.000	0.000
	Atom 3	0.000	0.230	0.000
	Atom 4	0.000	0.770	0.000
	Atom 5	0.000	0.000	0.230
	Atom 6	0.000	0.000	0.770

of quaternary vanadium fluoride Rb$_2$NaVF$_6$. The structural properties are predicted by applying the GGA-PBEsol [13], while the electronic structures and magnetic properties are calculated with GGA-PBEsol along with TB-mBJ exchange potential. In this study, we have chosen the following calculation parameters: the $K_{\max} = 9$ (RMT)$^{-1}$ ($K_{\max}$ is the plane wave cut-off, and RMT is the smallest of all atomic sphere radii). The Fourier expanded charge density was limited at $G_{\max} = 12$ (Ryd)$^{1/2}$, the $l-$expansion of the non-spherical potential and charge density was performed up to $l_{\max} = 10$. The cut-off energy is set to -7 Ryd to separate the core from valence states. The muffin-tin radii (MT) for Rb, Na, V and F to be 2.50, 1.98, 1.78 and 1.69 atomic units (a.u.), respectively. The iteration process is repeated until the calculated total energy and charge of the crystal converge to less than 0.0001 Ryd and 0.001e, respectively.

3. Results and discussion

3.1. Stability and structural properties

In 1966, R. Hoppe studied the crystallography of the compound Rb$_2$NaVF$_6$ [19,20]. The quaternary vanadium fluo-

ride Rb$_2$NaVF$_6$ crystallizes in the cubic NaCl (B1) structure with a space group of (Fm$\bar{3}$m) (no. 225). Figure 1 and Table I exhibit the crystal structure and the Rb, Na, V, and F atoms positions of Rb$_2$NaVF$_6$, respectively. We have optimized the Rb$_2$NaVF$_6$, with and without spin-polarized calculations. We have computed the total energies corresponding to the unit cell volumes and fitted to the Birch-Murnaghan's equation of state (EOS) [21] to verify the phase stability of the compound. And evaluate the structural properties such as the equilibrium lattice constant a, bulk modulus B and the
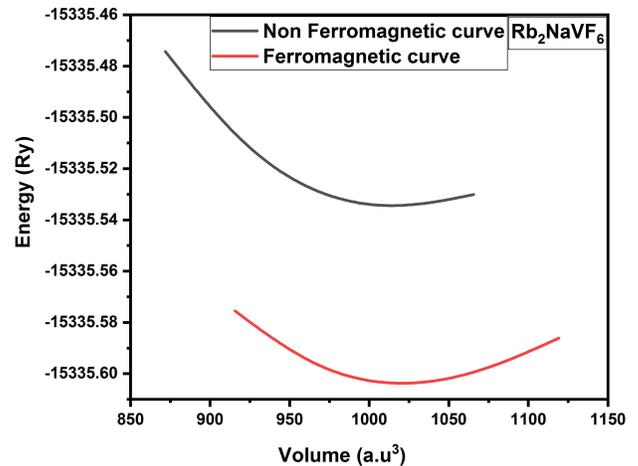
FIGURE 2. Volume optimization curve of quaternary vanadium fluoride Rb$_2$NaVF$_6$.

TABLE II. Calculated lattice constant (a), bulk modulus (B), pressure derivative B', minimum equilibrium energy E_0, and equilibrium volume V_0 of Rb$_2$NaVF$_6$.

a (Å)	B (GPa)	B'	Energy E_0 (Ry)	Volume V_0 (a.u^3)	character
8.4499, 8.46 [19,20]	69.4580	5.2094	-15335.605695	1017.8553	Ferromagnetic
8.4339, 8.46 [19,20]	70.7549	4.6757	-15335.536252	1012.1034	Non-magnetic

bulk modulus pressure derivative B', the inspected structural constants of Rb_2NaVF_6 are recapitulated in Table II, our results are in good agreement with the obtainable theoretical and experimental data. By comparing the two curves, it is obvious that the ferromagnetic curve is below the non-magnetic curve, which indicates that the Rb_2NaVF_6 structure is stable in ferromagnetic phase. The energy verses volume curves are shown in the Fig. 2.

3.2. Electronic, magnetic properties and half-metallic comportment

In this section, we have predicted the electronic band structure, total (TDOS), and partial (PDOD) densities of states for Rb_2NaVF_6, using GGA-PBEsol [13] accompanying with (TB-mBJ) of Tran-Blaha modified Becke-Johnson approximation [14,22]. Figures 3 and 4 exhibit the band structure of Rb_2NaVF_6 for spin-up and spin-down, respectively. It is apparent in Fig. 3 that the highest valence band is above the Fermi level, hence the metallic behavior of the structure. For Fig. 4, we mark two gaps, the half-metallic ferromagnetic

gap (G_{HMF}) and the half-metallic gap (G_{HM}), G_{HMF} is the energy difference between the valence-band maximum (VBM) and conduction-band minimum (C_{BM}) [4]. Rb_2NaVF_6 compound has a direct half-metallic ferromagnetic gap at $\Gamma - \Gamma$ of 7.837 eV and large half-metallic gap at $\Gamma - \Gamma$ high-symmetry point of 3.582 eV. The non-zero values of the half-metallic gap for Rb_2NaVF_6 demonstrate it to be true half-metallic ferromagnets and making it promising materials for employment in spintronic applications.

To know the origin of the ferromagnetic and the half-metallic behavior, we have calculated the densities of states (DOS) around the Fermi level (EF). Fig. 5 shows the total densities of states of Rb_2NaVF_6, Rb, Na, V, and F atoms. We notice that the total density of states (TDOS) is symmetrical

FIGURE 5. Spin-polarized total densities of states (TDOS) of Rb_2NaVF_6. The Fermi level is set to zero. (vertical dotted red line).

FIGURE 3. Spin-up band structure obtained with TB-mBJ for Rb_2NaVF_6.
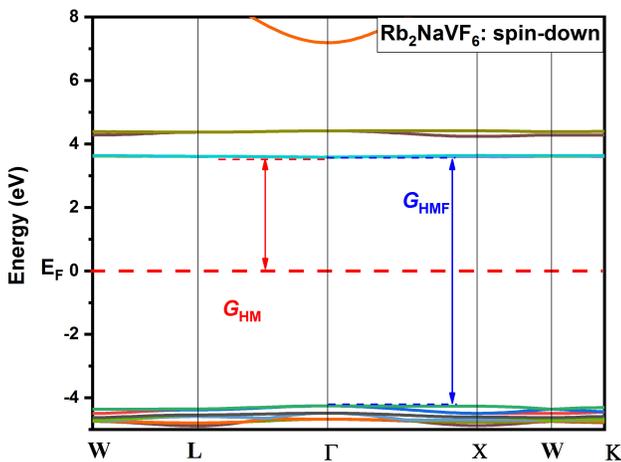
FIGURE 4. Spin-down band structure obtained with TB-mBJ for Rb_2NaVF_6.
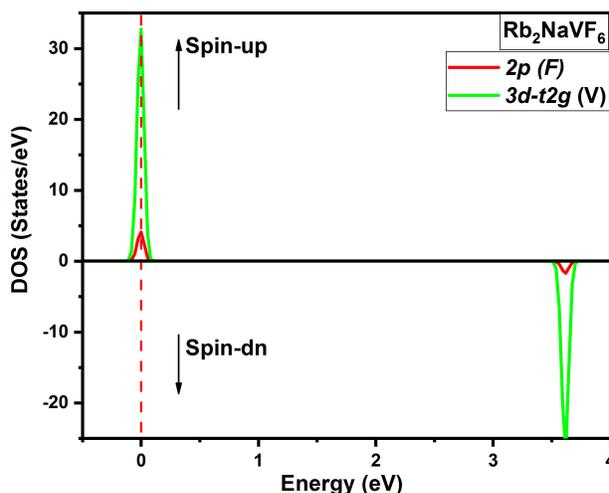
FIGURE 6. Spin-polarized partial densities of states (PDOS) of Rb_2NaVF_6. The Fermi level is set to zero. (vertical dotted red line)

TABLE III. Calculated total and local magnetic moments of the relevant Rb, Na, V, and F atoms and in the interstitial sites (in Bohr magneton μB) for Rb_2NaVF_6.

Compound	Total (μB)	Rb (μB)	Na (μB)	V (μB)	F (μB)	Interstitial (μB)
Rb_2NaVF_6	2.00001	0.00018	0.00009	1.71792	0.00495	0.25194

TABLE IV. Calculated $p-d$ exchange splitting $\Delta_x^v(pd) = E_v^\downarrow - E_v^\uparrow$ and $\Delta_x^c(pd) = E_c^\downarrow - E_c^\uparrow$, and exchange constants $N_0\alpha$ and $N_0\beta$ for Rb_2NaVF_6.

Compound	$\Delta_x^c(pd)$ (eV)	$\Delta_x^v(pd)$ (eV)	$N_0\alpha$	$N_0\beta$
Rb_2NaVF_6	3.584	0.013	41.724	0.151

except at Fermi level (0 eV) for spin-up and 3.618 eV for spin-down. The total densities of states are dominated by Rb between the energy from -11.102 and -10.694 eV, and at energy more than 8 eV. While the F dominates at an energy between -6.476 and -4.190 eV. Moreover, V dominates the peaks, which are at the energies 0, 3.618, and 4.380 eV. The half-metallic nature can be seen in the channel spin-down. To comprehend the source of the half-metallic gap and the half-metallic ferromagnetic gap we have plotted the partial densities of states. Figure 6 represent the partial densities of states of Rb_2NaVF_6, the pike located at the 0 eV (Fermi level) and 3.618 eV are mainly formed by the $3d - t2g$ (V) and 2p (F) states. The TDOS of Rb_2NaVF_6 depicted asymmetrical states of spin-up and spin-down due to strong $p-d$ hybridization between the $2p$ (O) and $3d - t2g$ (V) states around the Fermi level for the majority-spin direction. This hybridization occurs mainly at the top of the majority-spin valence bands and crosses the Fermi level, leading to the metallic nature for Rb_2NaVF_6 compounds, with spin polarization of 100% by using the following expression [23]:

$$p = \frac{N\uparrow(E_F) - N\downarrow(E_F)}{N\uparrow(E_F) + N\downarrow(E_F)} \times 100\%, \qquad (1)$$

where P is the spin polarization, $N\uparrow(E_F)$ and $N\downarrow(E_F)$ are the densities of states of the majority spin and minority spin around the Fermi level, respectively. Table III display the total and local magnetic moments of Rb_2NaVF_6. To interpret the implications of the $p-d$ interchange phenomenon on the magnetic behavior, we have calculated the total and local magnetic moments of the Rb, Na, V, and F atoms as well as the interstitial sites. The results exhibit the total magnetic moment for the Rb_2NaVF_6 compound was around 2 μB, usually caused by the V atoms' the local magnetic moment. $3d$ (V) majority-spin states, which are partially occupied with three electrons, resulting in a total magnetic moment of 2 μB. Otherwise, the calculated magnetic moment of the V atom is reduced to 1.71792 μB and minor local magnetic moments are induced at Rb, Na, F, and interstitial sites overdue to the $p-d$ exchange interaction between $2p$ (F) and $3d - t2g$(V) states. Important parameters established on band structures such as $p-d$ exchange splitting have also been calculated, $\Delta_x^c(pd) = E_v^\downarrow - E_v^\uparrow$ and $\Delta_x^c(pd) = E_c^\downarrow - E_c^\uparrow$ and the $s-d$

exchange constants $N_0\alpha$ (conduction band) and the $p-d$ exchange constant $N_0\beta$ (valence band).

Both $N_0\alpha$ and $N_0\beta$ parameters are calculated employing the mean-field theory whose expression is as follows [24,25]:

$$N_0\alpha = \frac{\Delta E_c}{x\langle s\rangle}, \qquad (2)$$

$$N_0\beta = \frac{\Delta E_v}{x\langle s\rangle}, \qquad (3)$$

where $\Delta E_c = E_c^\downarrow - E_c^\uparrow$ is the conduction band-edge spin-splitting and $\Delta E_v = E_v^\downarrow - E_v^\uparrow$ is the valence band-edge spin-splitting of Rb_2NaVF_6 at high symmetry point Γ. $\langle s\rangle$ is the half total magnetic moment per vanadium atom and x is the concentration of V in the structure. Table IV exhibits the calculated $p-d$ exchange splitting and exchange parameters. The positive $N_0\alpha$ constant indicates the ferromagnetic coupling between the $3d$ states of V and conduction bands. Also, we have calculated an important property of spin-polarized materials, the $\Delta_x^v(pd)$ and $\Delta_x^c(pd)$ parameters, which determines the attraction character in the Rb_2NaVF_6. However, the positivity $\Delta_x^v(pd)$ of Rb_2NaVF_6 structure means that the potential of minority spin is effective compared to the majority spin [26,27].

4. Conclusion

We have theoretically calculated the structural, electronic, and magnetic properties of the cubic Rb2NaVF6 system, using the density functional theory and it is concluded that:

- The lattice constant is in good agreement with the obtainable experimental data.

- Rb_2NaVF_6 is metallic for the majority spin states while semiconducting for the minority spin state with a direct large half-metallic gap of 3.582 eV.

- Rb_2NaVF_6 exhibits 100% spin polarization at the Fermi level (EF).

- The Rb_2NaVF_6 compound can be used in spintronic applications and can operate at a higher temperature due to its half-metallic properties and with a wide bandgap.

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