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Exploring ferromagnetic half-metallic nature of Cs_2NpBr_6 via spin polarized density functional theory*

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By employing the spin resolved density functional theory, half-metallic character is investigated in Cs_2NpBr_6 having a K_2PtCl_6-type structure. The results precisely predict the half-metallic behavior of Cs_2NpBr_6. In spin-down state it presents an indirect band gap, while in spin-up channel it turns metallic. The structure optimization confirms the half-metallic nature in ferromagnetic configuration. The calculated magnetic moment is 3 μ_B toward which the main contributor is the Np atom. Furthermore, all the computed results are compared with the available experimental and theoretical values. According to the present analysis, we recommend Cs_2NpBr_6 for spintronic applications.

Keywords: half-metallic, ferromagnetic, magnetic moment, spintronics

PACS: 61.82.Fk, 71.15.Mb, 75.30.Et, 75.50.Gg **DOI:** 10.1088/1674-1056/ab7da4

1. Introduction

Spintronics is basically different from conventional electronics, where besides the state of charge, the spin channels of electrons are also used as an additional degree of freedom for the efficiency of data transfer and storage. Therefore, spintronic devices (such as the spin valve, the spin current diode, spin tunneling devices, and the spin filter) require greatly spin-polarized current insertion into semiconductors.[1–3] However, presently, the major problem is that the spin based polarizability is insufficient for the insertion into semiconductors, which makes it an important aspect of research to find out high spin-polarized materials. In this perspective, the half-metallic ferromagnetic semiconductors are considered to be ideal, because they have metallic nature in one spin state and semiconducting (or insulating) character in the other spin channel, resulting in 100% spin polarizability at Fermi level as shown in Fig. 1.[4,5]

The first ferromagnetic half-metallic compound, NiMnSb, was predicted by de Groot *et al.*[6] in 1983. After that, many other systems owing half-metallic ferromagnetism were predicted theoretically or confirmed experimentally. These systems included full- and half-Heusler alloys, dilute magnetic semiconductors, metallic oxides, perovskite materials, chalcogenides and pnictides of transition metals.[7–10] Recently, half-metallic ferromagnetism has been investigated in cubic perovskite-related inorganic K_2PtCl_6-type materials. Faizan *et al.*[11] reported that K_2MoCl_6 and Cs_2MoCl_6 both have metallic nature in spin-down channel while semiconducting nature in spin-up states. Also, Faizan *et al.*[12] explored Cs_2MnF_6 as a half-metallic ferromagnet. Therefore, we were motivated to carry out an investigation on Cs_2NpBr_6. There are limited experimental and theoretical studies relevant to Cs_2NpBr_6. Magette and Fuger[13] prepared it by precipitation from a saturated solution of hydro-bromic containing CsBr and quadrivalent neptunium. From the x-ray powder diffraction pattern analysis, they reported that it possesses a face center cubic structure the same as K_2PtCl_6 with lattice constant 11.0820 Å and space group $Fm3m$. Brik and Vityak[14] used an analytical technique and calculated its lattice constant to be 11.02 Å. Sidey[15] also analytically calculated the lattice constant for Cs_2NpBr_6 to be 10.97 Å.

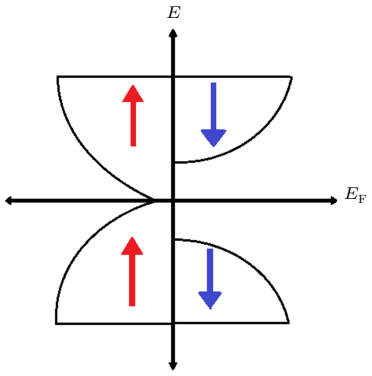


Fig. 1. Schematic dependence of spin polarization on energy in half-metallic ferromagnets.

As discussed above, scientific literature shows a gap for physical properties of Cs_2NpBr_6 on experimental and theoretical sides. To solve this discrepancy, we investigate the structural, electronic, and magnetic properties of Cs_2NpBr_6 by using the highly accurate spin-dependent density functional theory integrated with the full potential linearized augmented

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plane wave method.[16] We hope that our efforts will motivate experimenters to further analyze the Cs_2NpBr_6 for its technological applications.

2. Method of calculations

The present calculations are performed by using the spin-polarized density functional theory (DFT) implemented in Wien2k code[17] with the help of full potential linearized augmented plane wave method. In the calculations, the available information about Cs_2NpBr_6 is utilized, for example, it crystallizes into a face-center-cubic structure with space group $Fm3m$. In this structure, each unit cell consists of four formula units. The Cs, Np, and Br are positioned at (0, 0, 0), (1/4, 1/4, 1/4), and (0.24, 0, 0), respectively, in a unit cell (Fig. 2).[13] Furthermore, according to the requirements for Wien2k, the maximum value of the angular momentum vector (l_{max}), the product of the cut-off wave factor (K_{max}) with the smallest muffin-tin radius (RMT), and the number of k points in the first Brillion zone are taken to be 12, 7, and 1000, respectively, for proper convergence of energy. The RMT values of 2.4, 2.5, and 1.95 are assigned to Cs, Np, and Br, respectively. Moreover, the exchange correlation potential is treated in the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzehof[18] and GGA $+U$ (Hubbard parameter).[19]

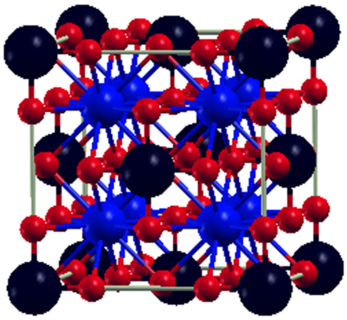


Fig. 2. Crystal structure of Cs_2NpBr_6, where blue, black, and red balls represent Cs, Np, and Br atoms, respectively.

3. Results and discussion

The calculated structural, electronic, and magnetic properties of Cs_2NpBr_6 are discussed in detail in this section. In Subsection 3.1, the magnetic and thermodynamic stabilities of the compound are discussed. In Subsection 3.2, our calculated results are compared with other results available from the literature. In Subsection 3.3, the electronic properties including electronic band structure, spin polarizability, and density of states are investigated. In Subsection 3.4, the magnetic properties of the studied compound are elaborated.

3.1. Magnetic and thermodynamic stabilities

The ground state stability on the basis of magnetic nature is checked by optimization process. The volume of unit cell is varied in a range from -10% to 10% of the experimental volume and the energy for each volume is noted. These calculations are carried out each time by considering Cs_2NpBr_6 as nonmagnetic, ferromagnetic, and anti-ferromagnetic. The anti-parallel spin alignments of Np are reserved for the anti-ferromagnetic configuration and parallel spins are kept aligned in the same direction for the ferromagnetic phase, while for the non magnetic configuration no spin polarized calculations are adopted. Then, the obtained volumes and energy values are plotted by taking the volume to be independent and energy to be dependent parameters as shown in Fig. 3. It can be seen from the figure that the compound has minimum energy when considering its ground state as being ferromagnetic. Therefore, it is ferromagnetic in the lowest energy state.

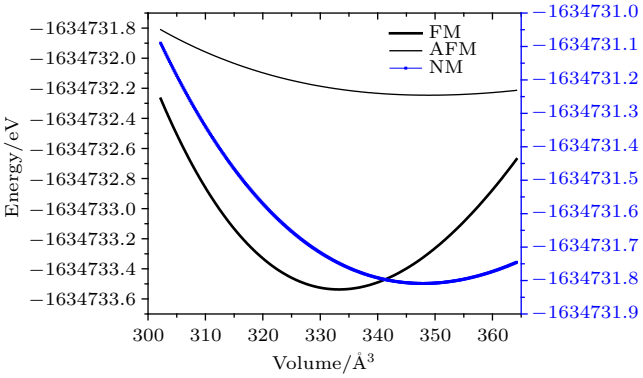


Fig. 3. Ground state stability of Cs_2NpBr_6 based on magnetic nature.

The thermodynamic stability is examined on the basis of formation energy by the following relation (taking idea from[20]):

$$\Delta H_f = E_{tot}(Cs_2NpBr_6) - xE_{Cs} - yE_{Np} - zE_{Br}, \qquad (1)$$

where E_{tot}, E_{Cs}, E_{Np}, and E_{Br} (Table 1) are the optimized ground state energies of Cs_2NpBr_6, Cs, Np, and Br, respectively; x, y, and z are the numbers of Cs, Np, and Br atoms in a unit cell of Cs_2NpBr_6. It can be clearly seen from Table 1 that ΔH_f has a negative value. Therefore, the formation reaction for Cs_2NpBr_6 is exothermic which is the evidence for its thermodynamic stability in ground state. Furthermore, our calculated values are in reasonable agreement with the experimental results available from the literature.[13]

Table 1. Calculated optimized energies of Cs, Np, Br and Cs_2NpBr_6, and formation energy (ΔH_f) for Cs_2NpBr_6.

	E_{Cs}/Ry	E_{Np}/Ry	E_{Br}/Ry	E_{tot}/Ry	ΔH_f
Present	−15580.510629	−57759.135485	−5213.208039	−120200.995241	−1.590382 Ry, −2088.01 kJ/mol
Exp.	–	–	–	–	−1862.5 kJ/mol[13]

3.2. Structural parameters

The following Murnaghan equation of state[20] is used for calculating the structural parameters such as lattice constant (a_0), bulk modulus (B), variation of bulk modulus with pressure (B'), volume (V_0), and ground state energy (E_0) in stability phase:

$$E(V) = E_0 \frac{BV}{B'}\left[\frac{(V_0/V)^{B'}}{B'-1}+1\right] - \frac{BV_0}{B'-1}. \quad (2)$$

By using Eq. (2), the relation between energy and volume for FM, AFM, and NM, calculated from the value obtained in the optimization process, is plotted in Fig. 3. To fit these plots in Fig. 3, the constants a_0, B, B', V_0, and E_0 are adjusted accordingly. These constants and the calculated lattice parameters are listed in Table 2.

The computed high bulk modulus reflects Cs_2NpBr_6 as a harder and stiffer material. Our calculated lattice constant is only 0.1% overestimated compared to the available experimental result. This shows the reliability of our calculations. Additionally, we also calculate the bond lengths and compare these with the experimental values in Table 2.

Table 2. Calculated lattice constant a_0, bulk modulus B, variation of bulk modulus with pressure B', volume V of the formula unit, ground state energy E_0, and bond lengths (Np–Br, Cs–Br) along with results available from the literature.

Method	a_0/Å	B/GPa	B'	V/Å^3	E_0/eV	Np–Br/Å	Cs–Br/Å
Present	11.0921	38.43	5	333.56	−1634733.535	2.82	3.98
Exp.	11.0820[13]	–	–	–	–	2.77[13]	3.92[13]
Theo.	11.02[14], 10.97[15]	–	–	–	–	–	–

3.3. Electronic profile

After the verification of ground state stability in ferromagnetic phase, the spin resolved band structures of Cs_2NpBr_6 are calculated along the high symmetrical directions in the first Brillouin zone and depicted in Fig. 4. Usually, in the predictable DFT calculations based on the GGA approximation and the LDA approximation, the strong interaction of on-site correlation is ignored and the electronic system is considered as being non-interactive.[22,23] Thus the electronic properties of magnetic materials are understimated. The K_2PtCl_6-type materials consist of heavy elements like actinides or lanthanides. Therefore, to treat the on-site correlation, we utilize the GGA + U approximation in addition to the GGA. The electrons localized in the f orbital of Np atom are considered as valence electrons by taking the value of U to be 0.26 Ry, for which Cs_2NpBr_6 is stable in both spin channels. From Fig. 4, it is clearly seen that the electronic states in the spin up configuration cross the Fermi level and replicate the metallic behavior, and in the spin-down channel the occupation of states on Fermi level is unavailable, which shows the semiconducting response. Similar behaviors can be seen from the plot for the density of states in Fig. 5, confirming that the resulting half-metallic response of Cs_2NpBr_6 is due to the spin polarizability. The amount of spin polarizability (P) can be estimated from the following relation:[24]

$$P = \frac{N(\uparrow)-N(\downarrow)}{N(\uparrow)+N(\downarrow)} \times 100\%, \quad (3)$$

where $N(\uparrow)$ and $N(\downarrow)$ represent the DOS at Fermi level in spin-up state and in spin-down state, respectively. The obtained P is 100%, signifying the maximum spin polarization in our investigated material. Furthermore, herein, the band gap in the spin-down channel is an indirect band gap with a value of 2.9 eV in the case of GGA and 3.4 eV in the case of GGA + U. As the valence band maximum lies at symmetry point Γ, while the conduction band minimum lies at symmetry point L.

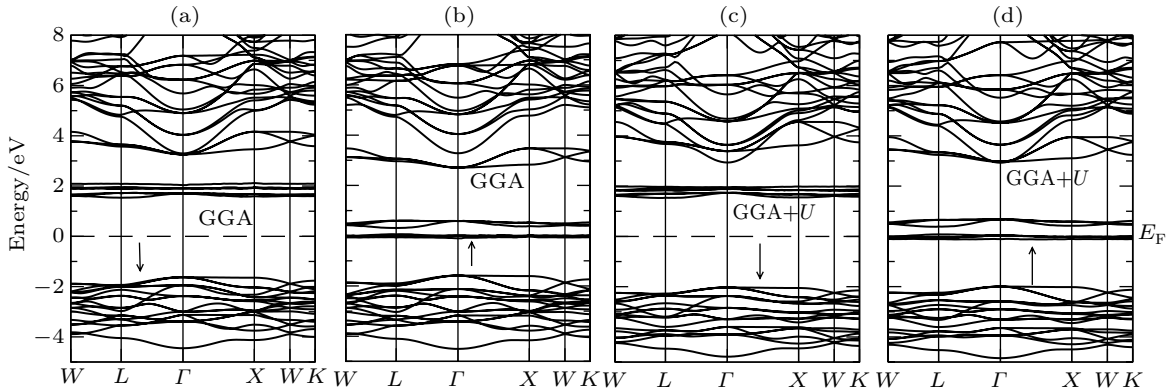


Fig. 4. Spin-polarized band structure of Cs_2NpBr_6 within (a), (b) GGA and (c), (d) within GGA + U.

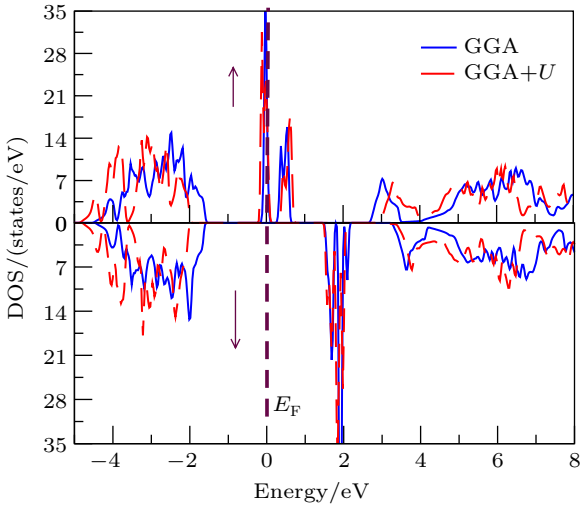


Fig. 5. Spin-polarized total DOS for Cs_2NpBr_6 within GGA and within GGA + U.

To further investigate the electronic structure on the basis of orbitals of constituent atoms, the spin-polarized partial DOS is calculated and illustrated in Fig. 6. The calculations with GGA and GGA + U show the same trend here, therefore, we present only partial DOS calculated via the GGA + U. In this figure, the partial DOS plots can be divided into three regions. The first region (from −5 eV to – 2 eV) is mainly occupied by Br-p states with minor contribution of Cs-p and Np-d states in both spin states. The second region (from −2 eV to 2 eV) contains the states responsible for the half-metallic nature. In the spin-up configuration, the Np-f states occupy the Fermi level, making Cs_2NpBr_6 metallic. The occupancy of these states with respect to the total DOS is 100%. In the spin-down state, Np-f shifts in the conduction band, leaving the Fermi level completely unoccupied. As a result, the electronic nature of the compound changes into that of semiconductor. Overall, the Np-f orbitals are responsible for the half-metallic behavior. Finally, the third region (2–8 eV) has Cs-d states in majority in collaboration with all other states in minority.

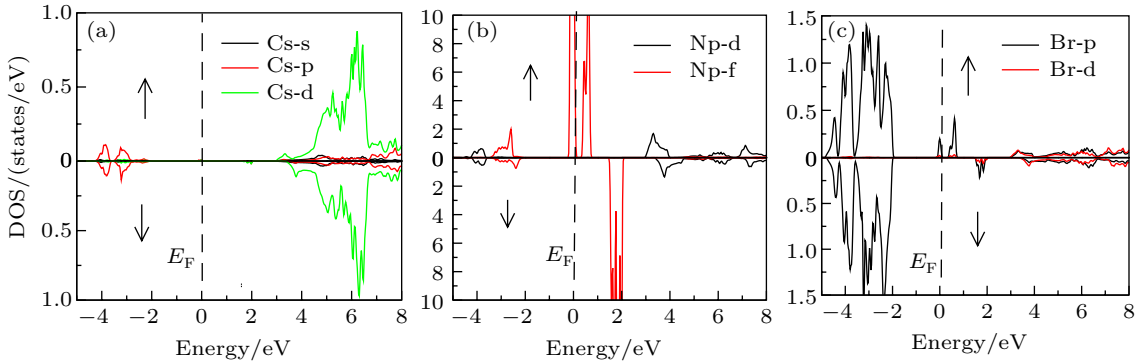


Fig. 6. Spin-polarized partial DOSs for Cs_2NpBr_6 within GGA + U.

3.4. Magnetic properties

The Cs_2NpBr_6 (51 valence electrons system) has an unpaired valence electron. Therefore, it exhibits magnetism due to the spin of the unpaired electron. This magnetism is of ferromagnetic nature as proved in the optimization process. The exchange interaction between atoms is one of the elementary sources of magnetic properties in ferromagnetic and anti-ferromagnetic materials. The exchange interaction includes the super exchange and the double exchange interactions. The super exchange interaction is responsible for anti-ferromagnetism while the double exchange for ferromagnetism.[25] The magnetic behavior of the studied bromide arises from the double exchange mechanism between Np–Np via bromine. In addition, the ferromagnetic strength is calculated via total magnetic moment M_{tot} in the GGA and GGA + U, where M_{tot} is the sum of magnetic moments of the constituent atoms (M_{Cs}, M_{Np}, and M_{Br}) and interstitial atoms (M_{inst}). All the computed values are listed in Table 3. It is clear that the main contributor toward the total magnetic moment is Np while the remaining part is contributed by the interstitial atoms and Cs atom. M_{tot} has a digit value of 3 μ_B in every case. This integral value of M_{tot} also approves the half-metallic behavior in the material because the half-metallic compounds are believed to have magnetic moment in integer.[26,27] The GGA + U slightly increases the magnetic moment of Np atom by treating its 5f electrons but the value of M_{tot} remains constant. As discussed in the introduction, such a type of spintronic material is proficient in utilizing the magnetic moments due to spin rather than electronic charge to transmit and store information.

Table 3. Calculated magnetic moment (in μ_B) of interstitial region (M_{inst}), Cs (M_{Cs}), NP (M_{Np}), Br (M_{Br}), and Cs_2NpBr_6 (M_{tot}).

Method	M_{inst}	M_{Cs}	M_{Np}	M_{Br}	M_{tot}
GGA	0.21612	0.0005	3.0780	−0.0443	3.0000
GGA + U	0.2038	0.0008	3.0312	−0.0403	3.0000

4. Conclusion

In this work, the full spin-polarized density functional theory is used to study the structural, electronic, and magnetic properties. The plots obtained through optimization pro-

cess show that Cs_2NpBr_6 is the most stable in ferromagnetic ground state. The computed structural parameters are found to be in excellent agreement with the results available from the scientific literature. The compound is found to be 100% spin polarized at Fermi level. The spin polarization makes it a semiconductor in spin-up configuration and metal in spin-down state. As a whole, its electronic behavior is confirmed to be half-metallic. The integral value of magnetic moment (3 μ_B) also confirms the ferromagnetic response of Cs_2NpBr_6. The f orbital electrons play a crucial role in determining the magnetic state of Cs_2NpBr_6. The half-metallic ferromagnetic nature can attract attention towards the growth of Cs_2NpBr_6 for spintronic applications.

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