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AB-INITIO CALCULATIONS OF STRUCTURAL, ELECTRONIC AND MAGNETIC PROPERTIES OF $LiRh_2Si_2$

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Abstract: *In this study, we investigated the structural, electronic and magnetic properties of the tetragonal $LiRh_2Si_2$ using the full-potential linearized augmented plane wave (FP-LAPW). The structural calculations were performed with four exchange and correlation potential (GGA- PBE, LDA-PW, GGA-WC and GGA-PBEsol), the electronic and magnetic properties were performed with GGA-PBE implemented in Wien2k code. We have obtained the cell dimensions, bulk modulus, and its pressure derivative. The calculated lattice parameters are in good agreement with experimental and previous theoretical results. We calculated cohesive energy as 4,95 eV/atom and $LiRh_2Si_2$ has good stability. Electron density plot of $LiRh_2Si_2$ shows strong covalent interactions between Si-Si and Rh-Si elements. We performed spin polarize calculation of Density of States (DOS). Electronic band chart that show $LiRh_2Si_2$ has metallic feature for both spin up and spin down configurations. The spin up and spin down electronic band chart nearly symmetric so the compounds has nonmagnetic feature. We searched pressure effect on magnetic moment of $LiRh_2Si_2$. The magnetic moment of $LiRh_2Si_2$ has been found 0.00075 (μ_B) and it decreased with increase of pressure.*

Key words: *$LiRh_2Si_2$, Ab-initio calculations, Wien2k, FPLAPW, structural properties, magnetic properties, electronic properties*

1. Introduction

Lithium-transition metal-tetrelides (tetr. = C, Si, Ge, Sn, Pb) are an interesting class of compounds with respect to crystal chemistry and lithium mobility. Although many compounds with quite expensive noble metals have been studied, they are important model compounds in order to understand the structure–property relationships. These materials have intensively been investigated in recent years with respect to their structural chemistry and potential use as electrode materials in lithium batteries [1]. Nano- and bulk-silicon have intensively been studied in recent years with respect to lithiation for use as alternative electrode materials in lithium-ion batteries [2].

$LiRh_2Si_2$ and LiY_2Si_2 have been synthesized and investigated for structural and bond peculiar of them. Some theoretical works performed to investigate structural and bond chemistry of these materials [3].

Steinberg and Schuster **(**1979) synthesized and structural characterized of LiY_2Si_2 and $LiNd_2Si_2$ ternary compounds [4].

When we focus on this class of compounds we can see same studies on synthesis and some works focus on determine the physical properties. There are less theoretical study on these compounds and physical properties of $LiRh_2Si_2$ have not been studied in detail. That's why we focus on this study.

2. Computational method

The structural, electronic and magnetic properties of $LiRh_2Si_2$ were investigated by means of FP-LAPW method by using Wien2k package [5]. The cutoff energy, which defines the separation of valence and core states, was chosen as -7 Ry. The Muffin-tin sphere radii were selected 2,26 a.u. for Li 2,32 a.u for Rh and 1,7 a.u. for Si. The convergence of the basis set was controlled by a cut off parameter $R_{mt}*K_{max}$ was used 7, where R_{mt} is the smallest of the MT sphere radii and K_{max} is the largest reciprocal lattice vector used in the plane wave expansion. The magnitude of the largest vector in charge density Fourier expansion (G_{max}) was 12. We select the energy convergence as 0.0001 Ry and charge convergence as 0.001 e during self-consistency cycles. In these calculations, we neglected the effect of spin orbit coupling. For the Brillouin zone (BZ) integration, the tetrahedron method [6] with 195 special k points in the irreducible wedge (3000 k-points in the full BZ) was used to construct the charge density in each self-consistency step.

The structural calculation were performed with four exchange and correlation potentials (GGA-PBE, LDA, GGA-WC and GGA-PBEsol) [7-10] as implemented in Wien2k code. We used GGA-PBE potential for electronic and magnetic calculations.

$LiRh_2Si_2$ has tetragonal lattice with 127 (P4/mbm) space group (Fig.1). The atomic positions and cell dimensions of compounds are given in Table 1 [1].

Table 1. Unit cell parameters of $LiRh_2Si_2$

Unit cell dimensions	a= 6,981	c= 2,746	
Atomic coordinates	**Li**	**Rh**	**Si**
	0, 0, 0	0.14937, 1/2 + *x*, 1/2	0.3542, 1/2 + *x*, 0

The calculations started with experimental data and searched for minimum energy depend of volume. The electronic and optical calculations were performed with optimized structure parameters.

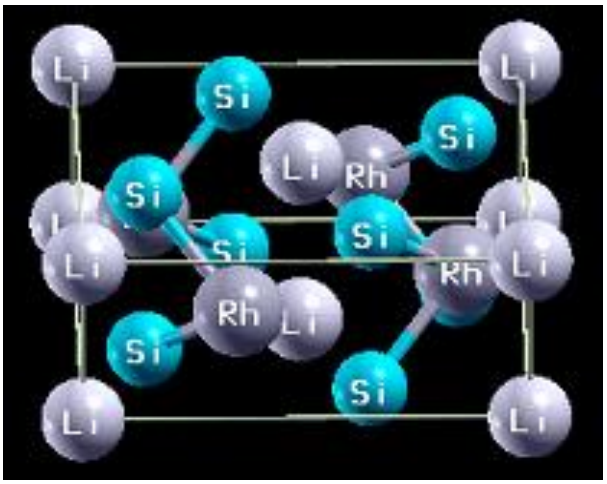


Figure 1. Unit cell of tetragonal $LiRh_2Si_2$ structure

3. Results and discussion

3.1. Structural properties

To find the ground state energy and optimize unit cell dimensions we calculate the total energy for diverse volume around experimental unit cell volume. The calculated total energies versus volume are fitted to the empirical Murnaghan's equation of state [11] to determine the ground state properties. The calculated total energy as a function of volume for four different potential and spin polarized PBE-GGA are plotted in Figure 2. We calculated ground state energy, unit cell volume, bulk modulus and derivative bulk modulus from structural optimization for each selected exchange correlation potentials. Calculated volume (V_0), bulk modulus (B_0), minimum energy (E) and derivative pressure (B') values are given in Table 2.

Table 2. Calculated structural parameters of $LiRh_2Si_2$

Values / Potentials	V_0 (au^3)	B_0 (GPa)	B' (GPa)	E (Ry)
Nonmagnetic GGA-PBE	925.1924	167.7183	4.4	-40633.075959
Spin polarize GGA-PBE	924.2944	169.1183	4.4	-40633.076791
Nonmagnetic LDA	879.7674	195.3441	4.5	-40588.207521
Nonmagnetic GGA-WC	903.2018	180.9338	4.6	-40626.066480
Nonmagnetic GGA PBEsol	898.1046	185.4190	4.6	-40609.797268

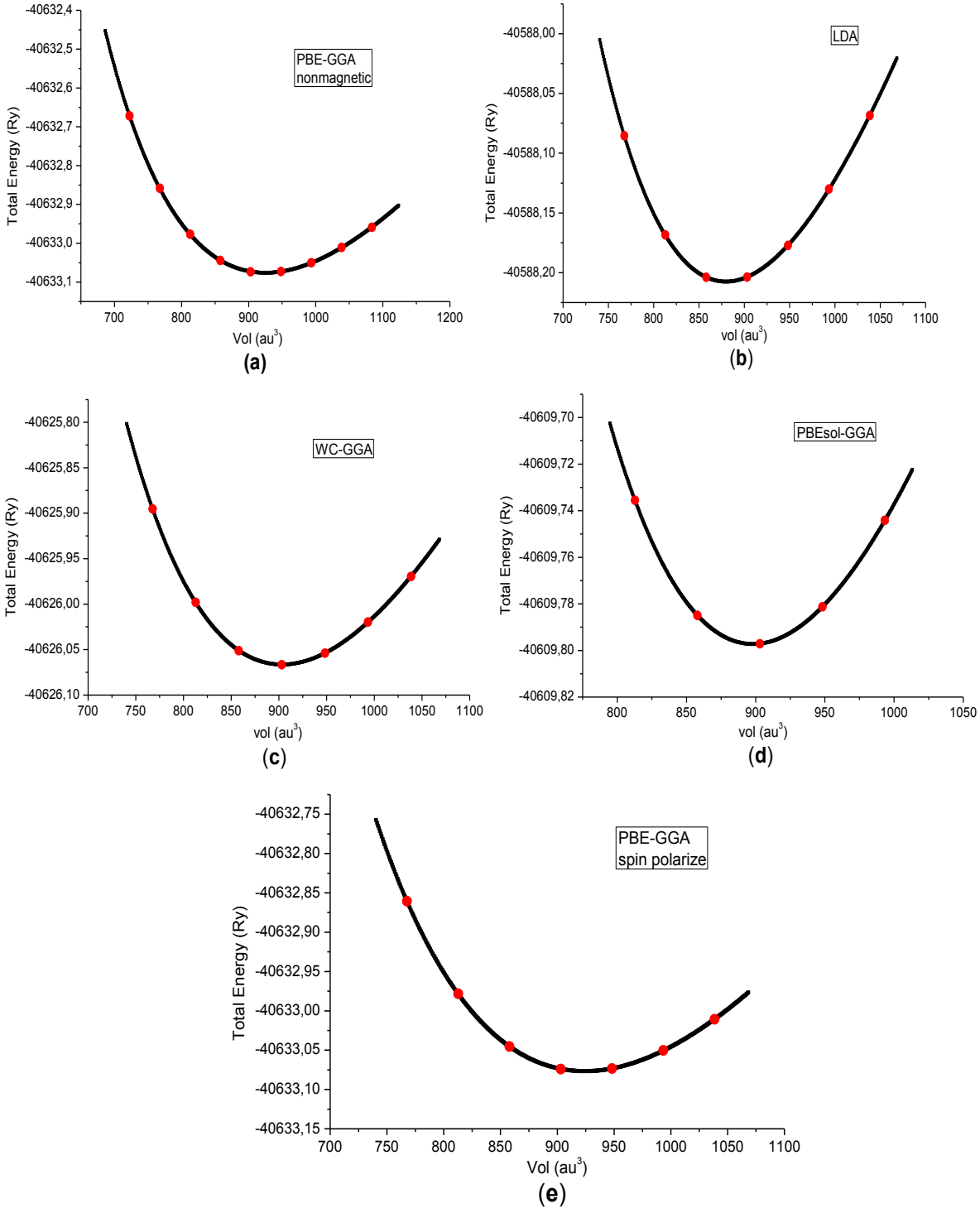


Figure 2. Dependence of total energy on unit cell volume of $LiRh_2Si_2$ with a) Nonmagnetic PBE-GGA, b) LDA, c) WC-GGA, d) PBEsol, e) Spin polarized PBE-GGA potentials

Experimental volume of $LiRh_2Si_2$ is 903,2 au^3 [1] and GGA-WC potential result is very close to it. Calculated bulk modulus has good agreement with previous calculated results, 200 GPa, in the LDA [1].

The structural stability of cell is confirmed by cohesive energy calculation. According to cohesive energy [12]

$$E_{coh} = -\frac{E^{tot}_{LiRh_2Si_2} - aE^{tot}_{Li} - bE^{tot}_{Rh} - cE^{tot}_{Si}}{a+b+c} \quad (1)$$

Where $E^{tot}_{LiRh_2Si_2}$, E^{tot}_{Li}, E^{tot}_{Rh}, E^{tot}_{Si} are total energy of $LiRh_2Si_2$ unit cell, isolated Li, Rh and Si atoms, respectively. a, b and c indexes refer to the number of each atoms in the cell. We obtained the value of cohesive energy as 4,95 eV/atom for tetragonal $LiRh_2Si_2$.

3.2. Electronic and magnetic properties

It is well known that the electronic band structure and density of states (DOS) are important quantities to determine the crystal structure [12, 13]. In order to understand bonding character clearly, the total and partial densities of states (DOS) is calculated in Figure 3. Calculated DOS for spin up and spin down is given in Figure 4 are nearly symmetric and $LiRh_2Si_2$ has metallic feature for both spin. We plotted an electronic band chart for spin up and spin down to understand the electronic properties of the structure (Fig.5). In this figure the Fermi energy level set to origin. Spin up and spin down band charts are nearly same and has metallic feature.

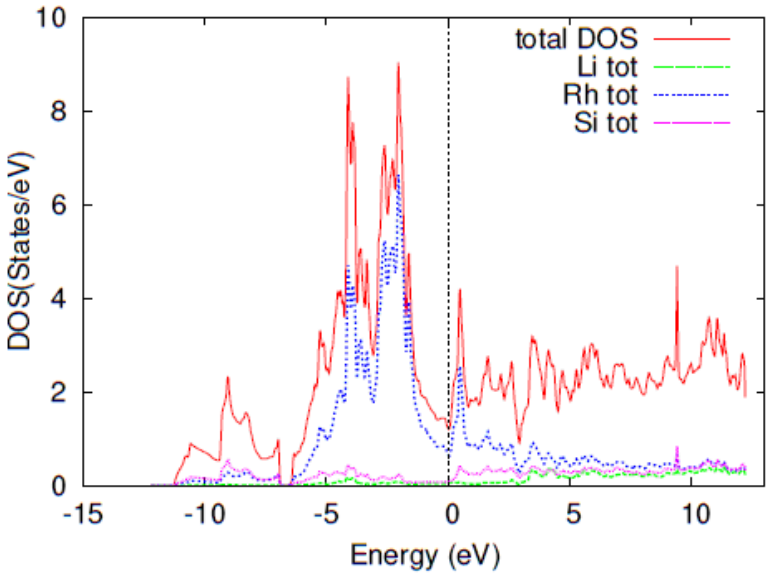


Figure 3. Calculated total and partial DOS of $LiRh_2Si_2$

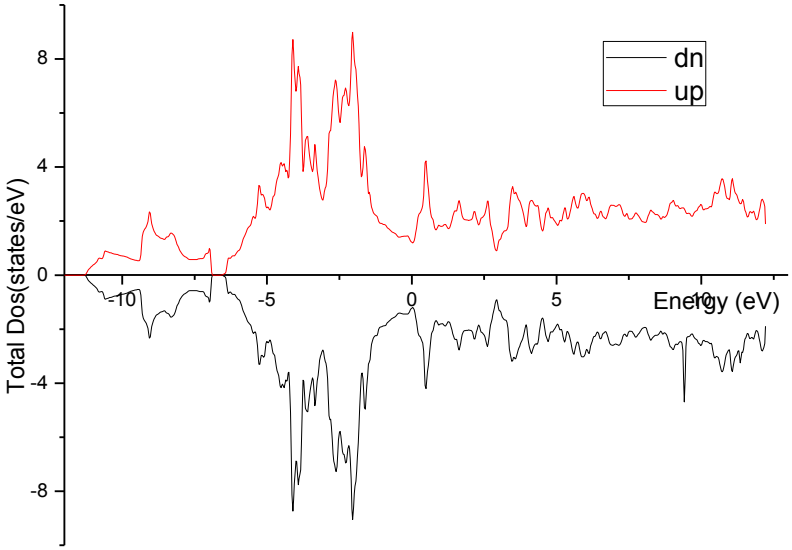


Figure 4. Density of states (DOS) of $LiRh_2Si_2$ with spin up and spin down configurations

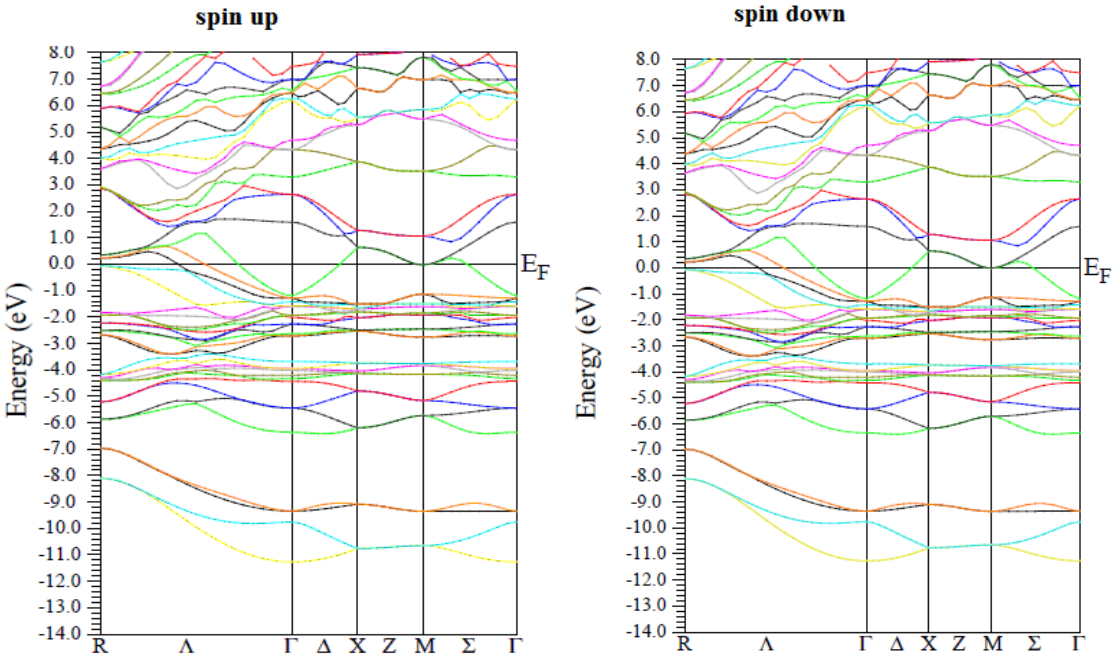
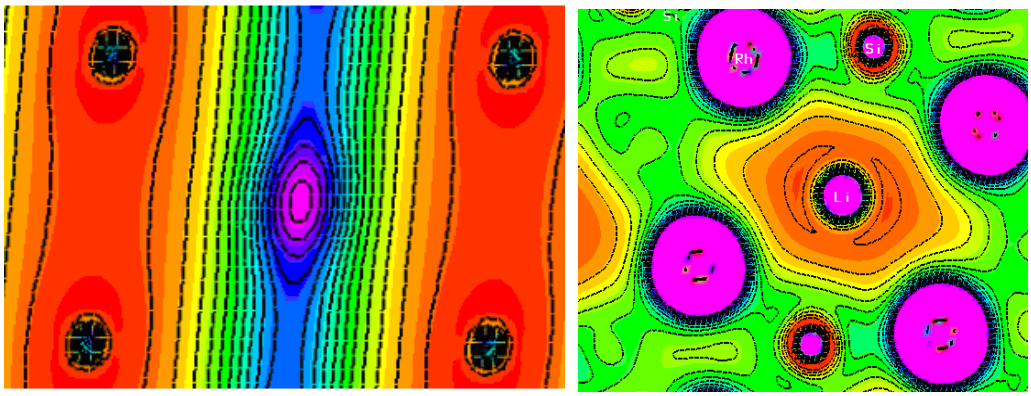


Figure 5. Band structure of $LiRh_2Si_2$ with (a) spin up and (b) spin down configurations.

We calculated electron density plots to understand bond characters of $LiRh_2Si_2$ in Figure 6. Charge distribution shows that there are strong covalent bond with Si-Si and Rh-Si elements.



(a) (b)

Figure 6. Electron density plot of $LiRh_2Si_2$ with (a) 100 plate (b) 110 plate

To study the magnetic properties of the intermetallic $LiRh_2Si_2$ compounds, spin polarized calculations with the GGA (PBE) were performed. The total, interstitial and local magnetic moments of the compounds under investigation are summarized in Table 3. The structure is paramagnetic with experimental cell dimensions and became diamagnetic with pressure.

Table 3. Calculated total, interstitial and local magnetic moments of the compounds with GGA-PBE

Pressure (Gpa)	m^{int}	m^{Li}	m^{Rh}	m^{Si}	m^{cell}
0	0.00042	-0.00049	0.00027	0.00005	0.00075
14.89	0.00030	-0.00019	-0.00002	-0.00002	-0.00023
25.3	-0.00188	-0.00096	-0.00052	0.00002	-0.00578

4. Conclusions

We have searched structural, electronic and magnetic properties of tetragonal $LiRh_2Si_2$ structure using all electrons full potential linearized augmented plane wave (FPLAPW) method based on DFT within the generalized gradient approximation (GGA) implemented in Wien2k code. We calculated ground state energy unit cell dimensions and cohesive energy values. The calculated cell constants are good agreement with experimental and previous theoretical works. Calculated electron density plot and dos plot show that there are strong covalent bond with Si-Si and Si-Rh elements. The calculated electronic band structure shows that $LiRh_2Si_2$ has metallic character both with spin up and spin down

configuration. $LiRh_2Si_2$ show paramagnetic feature with experimental unit cell constants and became show diamagnetic feature with increasing the pressure.

Acknowledgment

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