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Investigation of structural, electronic, elastic and phonon properties of cubic spinel ZnM_2O_4(M = Co, Rh and Ir) compounds

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ABSTRACT

The results obtained from ab initio calculations on ZnM_2O_4 (M = Co, Rh and Ir) compounds have been reported. The elastic constants, Bulk, Shear and Young modulus, and Poisson's ratios of the compounds are presented. In addition, full phonon dispersion curves and projected density of states of the compounds have been computed using the direct method. The lattice parameters (*a*) and internal parameters (*u*) are found to be in a good agreement with experimental results. According to both the *B/G* values and the Poisson's ratio, these compounds have covalent bondings. The analysis of the band structure of these compounds have indicated indirect band gaps of 1.25 eV for $ZnCo_2O_4$ and 1.14 eV for $ZnRh_2O_4$ and 0.86 eV for $ZnIr_2O_4$. The full phonon spectra of these compounds show that they are dynamically stable in the cubic spinel structure.

1. Introduction

Transparent conductive oxides (TCOs) are electrically conductive materials in the visible region of the spectrum and have very low absorption of electromagnetic waves. These materials are usually synthesized using thin film technology and utilised in opto-electric circuit components such as solar cells and image screens. In addition, they can be manufactured as n-type or p-type conductive materials and have applications in opto-electronic technology which in turn provides saving of power in wide ranges of applications [1,2]. Other synthesis methods include scattering, reactive thermal deposition, chemical vapor deposition, laser ablation, and sol-gel method [3–7].

Zinc spinel ZnM_2O_4 (M = Co, Rh, Ir) compounds have been a great of interest in many experimental and theoretical works [8–29]. The structural and electronic properties of ZnM_2O_4 (M = Co, Rh, Ir) spinel compounds were calculated by Amini et al. using Heyd-Scuseria and Ernzerhof (HSE06) functions [8]. In their study, they found that the indirect band gap values for $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ compounds as 3.88, 2.91 and 2.53 eV, respectively. Volnianska et al. [9] examined the structural and electronic properties of spinel $ZnRh_2O_4$ compound using the density functional theory in the generalized gradient approach (GGA) with Quantum-Espresso code and reported a lattice constant of 8.67 Å for $ZnRh_2O_4$. Ramo et al. [11] investigated the influence of imperfections and irregularities on the electronic properties of Zn_2O_4 with the CRYSTAL09 package and the hybrid Becke three-parameter Lee–Yang–Parr (B3LYP) function. Dekkers et al. [13] measured the lattice constants of the p-type transparent conductive $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ oxides as 8.104 Å, 8.489 Å and 8.507 Å, respectively, using the X-ray diffraction method. In the same study, they measured the band gap values of $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ as 2,26 eV, 2,74 eV and 2,97 eV, respectively, by vibrating laser storage method. The lattice constant of spinel $ZnCo_2O_4$ was measured by XRD method and found to be 8.120 Å in an experimental study conducted by Sharma et al. [14]. The optical properties and electronic structure of $ZnRh_2O_4$ spinel have been investigated in an experimental study by Singh et al. [15] and the indirect band-gap for $ZnRh_2O_4$ was measured as 1.2 eV. The

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electronic and optical properties of ZnM_2O_4 (M = Co, Rh, Ir) spinel oxides have recently been studied by Samanta [25] using both PBE and Tran-Blaha modified Becke-Johnson density function. He found indirect band gap value for $ZnCo_2O_4$ as 0.773 eV with PBE and 3.354 eV with TB-mBJ function, for $ZnRh_2O_4$ as 0.897 eV with PBE and 2.53 eV with TB-mBJ function, for $ZnIr_2O_4$ as 0.416 eV with PBE and 2.32 eV with TB-mBJ function, respectively. Those studies in literature however do not present a full thorough investigation on these materials, for instance, the phonon spectrum of the solids are very important in determining various basic solid state properties such as thermal conductivity, thermal expansion, heat conduction, electron-phonon interaction, specific heat, and phase transition. The full phonon properties of $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ have not yet been studied using any theoretical or experimental method to best of our knowledge Thus, in this study, the phonon properties as well as the structural, elastic and electronic properties of $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ spinel compounds were investigated using the ab initio calculations of density functional theory (DFT). This work specifically focuses on the study of the full phonon spectrum of $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ spinel compounds using the direct method.

2. Method

Ab initio calculations were performed using plane wave pseudopotential density functional theory (DFT) as implemented in the code MedeA [30,31] with the projected augmented wave [32]. The generalized gradient approximation (GGA) of Perdew-Burke–Ernzerhof (PBE) [33] was chosen for exchange-correlation functional. An energy cutoff of 500 eV was found in the calculation of structural, elastic and phonon properties. Energy convergence criteria were set to 10^{-9} eV using the normal (blocked Davidson) algorithm and reciprocal space projection operators. The Brillouin was integrated using Monkhorst–Pack generated sets of k-points [34]. For the $ZnRh_2O_4$, $ZnIr_2O$ and $ZnCo_2O_4$ spinellars, $5 \times 5 \times 5$ and $6 \times 6 \times 6$ *k*-points meshes were found to be sufficient, respectively. Fermi level was smeared by Methfessel–Paxton type [35] with a width of 0.225 eV. Elastic constants were calculated using the stress-strain approximation [36], where stress due to an applied strain was directly calculated. Phonon spectra were obtained using the MedeA-Phonon in conjunction with MedeA-Vasp by the direct method. $1 \times 1 \times 1$ supercell containing 56 atoms for the spinel structure were used. The calculated specific heat capacity at constant volume (C_v) of zinc spinel ZnM_2O_4 (M = Co, Rh, Ir) compounds were calculated using the quasi harmonic approximation (QHA).

3. Results

3.1. Structural properties

ZnM_2O_4 (M = Co, Rh, Ir) are spinel oxides compounds, which belong to Fd-3m (227) space group. Spinel compounds are characterized by two structural constants. The first one is the lattice constant (a_0), the second is the internal parameter (*u*). The Zn atoms are located at tetrahedral positions 8a (1/8, 1/8, 1/8) at Wyckoff positions, while the M (Co, Rh, Ir) atoms are located at 16d (1/2, 1/2, 1/2) and O atoms are surface-centered cubic at 32e (u, u, u) [37]. The crystal structure of cubic spinel oxides ZnM_2O_4 (M = Co, Rh, Ir) is shown in Fig. 1. For spinel ZnM_2O_4 (M = Co, Rh, 1r) compounds, crystal structures were formed using the InfoMaticA Database included in the MedeA package program. Then the convergence value of the total energy for k points and the cut-off energy E_{cut} were found. The energies of these materials were 532 eV for $ZnCo_2O_4$, $ZnRh_2O_4$ compounds, 510 eV for $ZnIr_2O_4$ and the values of *k*-points were taken as $6 \times 6 \times 6$ $ZnRh_2O_4$ for $ZnCo_2O_4$ and $5 \times 5 \times 5$ for $ZnIr_2O_4$ compounds. The computed the

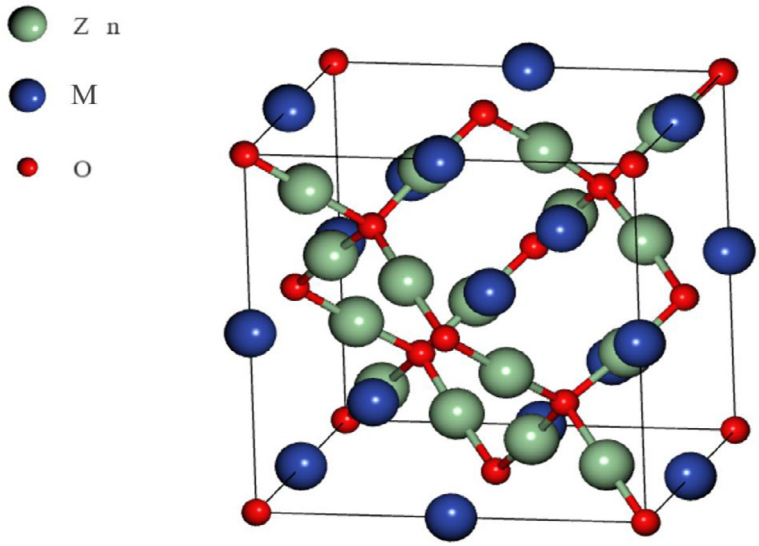

Fig. 1. The crystal structure of cubic spinel ZnM_2O_4 (M = Co, Rh, Ir) compounds.

Table 1
The computed lattice constants a (Å), internal structure parameters u and Bulk modulus B(GPa), Debye temperature Θ_D (K), elastic costants C_{ij} (GPa), Shear modulus G(GPa), B/G ratio, Young modulus E(GPa) and Poisson ratio ν of ZnM_2O_4 (M = Co, Rh, Ir) compounds.

Compounds	References	a	u	B	Θ_D	C_{11}	C_{12}	C_{44}	G	B/G	E	ν
$ZnCo_2O_4$	This work	8.159	0.2649	175.21	505,616	253.69	135.97	96.87	79.33	2.21	206.77	0.303
	[8]	8.02	0.264	–	–	–	–	–	–	–	–	–
	[13-Exp.]	8.104	–	–	–	–	–	–	–	–	–	–
	[14]	8.120	–	–	–	–	–	–	–	–	–	–
	[20]	8.0573	–	–	–	–	–	–	–	–	–	–
	[10]	8.176	0.264	–	–	–	–	–	–	–	–	–
	[24]	8.104	0.263		–	–	–	–	–	–	–	–
	[25]	8.176	0.264	210.34	–	–	–	–	–	–	–	–
	[26]	8.05	–	–	–	–	–	–	–	–	–	–
	[27-PBE]	8.17	–	–	–	–	–	–	–	–	–	–
	[27-HSE]	8.01	–	–	–	–	–	–	–	–	–	–
$ZnRh_2O_4$	This work	8.618	0.2599	190.59	384,991	255.86	157.96	61.36	59.05	3.40	153.15	0.366
	[8]	8.49	0.26	–	–	–	–	–	–	–	–	–
	[9]	8.67	–	–	–	–	–	–	–	–	–	–
	[13-Exp.]	8.489	–	–	–	–	–	–	–	–	–	–
	[15]	8.506	0.261	–	–	–	–	–	–	–	–	–
	[24]	8.489	0.263		–	–	–	–	–	–	–	–
	[25]	8.637	0.261	198.19	–	–	–		–	–	–	–
	[27-PBE]	8.57	–	–	–	–	–	–	–	–	–	–
	[27-HSE]	8.48	–	–	–	–	–	–	–	–	–	–
$ZnIr_2O_4$	This work	8.745	0.2598	181.09	281,557	250.56	146.35	44.99	47.71	3.79	131.58	0.379
	[8]	8.59	0.26	–	–	–	–	–	–	–	–	–
	[11]	8.77	–	–	–	–	–	–	–	–	–	–
	[13-Exp.]	8.507	–	–	–	–	–	–	–	–	–	–
	[24]	8.507	0.263		–	–	–	–	–	–	–	–
	[25]	8.759	0.262	207.43	–	–	–	–	–	–	–	–
	[27-PBE]	8.75	–	–	–	–	–		–	–	–	–
	[27-HSE]	8.59	–	–	–	–	–	–	–	–	–	–

internal parameter (u), lattice constants (a_0) for ZnM_2O_4 (M = Co, Rh, Ir) compounds are given in Table 1 and compared with previous experimental and theoretical studies [8–11, 13–15, 20–22, 24–27]. These calculated values are in a good agreement with the previously values. Moreover, the calculated internal parameters for spinel ZnM_2O_4 (M = Co, Rh, Ir) compounds were compared with the theoretical work Ref. [8], and the error values for $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ spinel compounds were found to be 0.35%, −0.03% and −0.07%, respectively. The calculated lattice constants in this study are compared with Ref. [21], the error values of the lattice constants were calculated as 0.68%, 1.63% and 2.79% for spinel $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ compounds, respectively. The computed values of the bulk modulus of spinel oxides compounds are predicted to be 175.21 GPa, 190.59 GPa, and 181.09 GPa for $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ compounds, respectively. These computed values are good agreement with available theoretical data [25].

3.2. Electronic properties

The electronic band structures along the high symmetry directions for spinel oxides ZnM_2O_4 (M = Co, Rh, Ir) compounds are presented in Fig. 2. From the electronic band structure graphs, the direct and indirect band gap values of these compounds are given in Table 2. Dekkers et al. [13] found that the values obtained in the study using the HSE06 method were in agreement with our work and that the indirect band gaps at Γ–X directions were 2.26 eV, 2.74 eV, 2.97 eV for $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ spinel compounds, respectively, and also Amini et al. [8] used the another method to find the indirect band gaps of $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ as 3.88 eV, 2.91 eV and 2.53 eV, respectively. The indirect band gap values for the three compounds are given in Table 2 with available data. Moreover, for better understanding of electronic band contribution of these compounds, the total and partial density of state curves of the compounds were obtained. The density of state curves obtained for spinel oxides $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ compounds are shown in Fig. 3. It can be seen from the densities of state that for the spinel $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ compounds, the main contributions below and above the band gap for three compounds came from electrons of the 3d and 2p orbitals. The Fermi energies of the compounds were calculated as E_F ($ZnCo_2O_4$) = 5.28 eV, E_F ($ZnIr_2O_4$) = 5.03 eV and E_F ($ZnRh_2O_4$) = 5.55 eV and the Fermi energy was taken as zero by subtracting from all other band energies. The indirect band gap for all three compounds, at Γ–X direction have been found to be different values with different methods.

3.3. Elastic properties

Elastic constants are significant parameters that describes the mechanical behaviour of a crystal and provide information about the strength and the structural stability of the material. There are three independent elastic constants such as C_{11}, C_{12} and C_{44} for cubic systems. The calculated values for Shear modulus (G), Bulk modulus (B) and Young's modulus (E), elastic anisotropy factors (A),

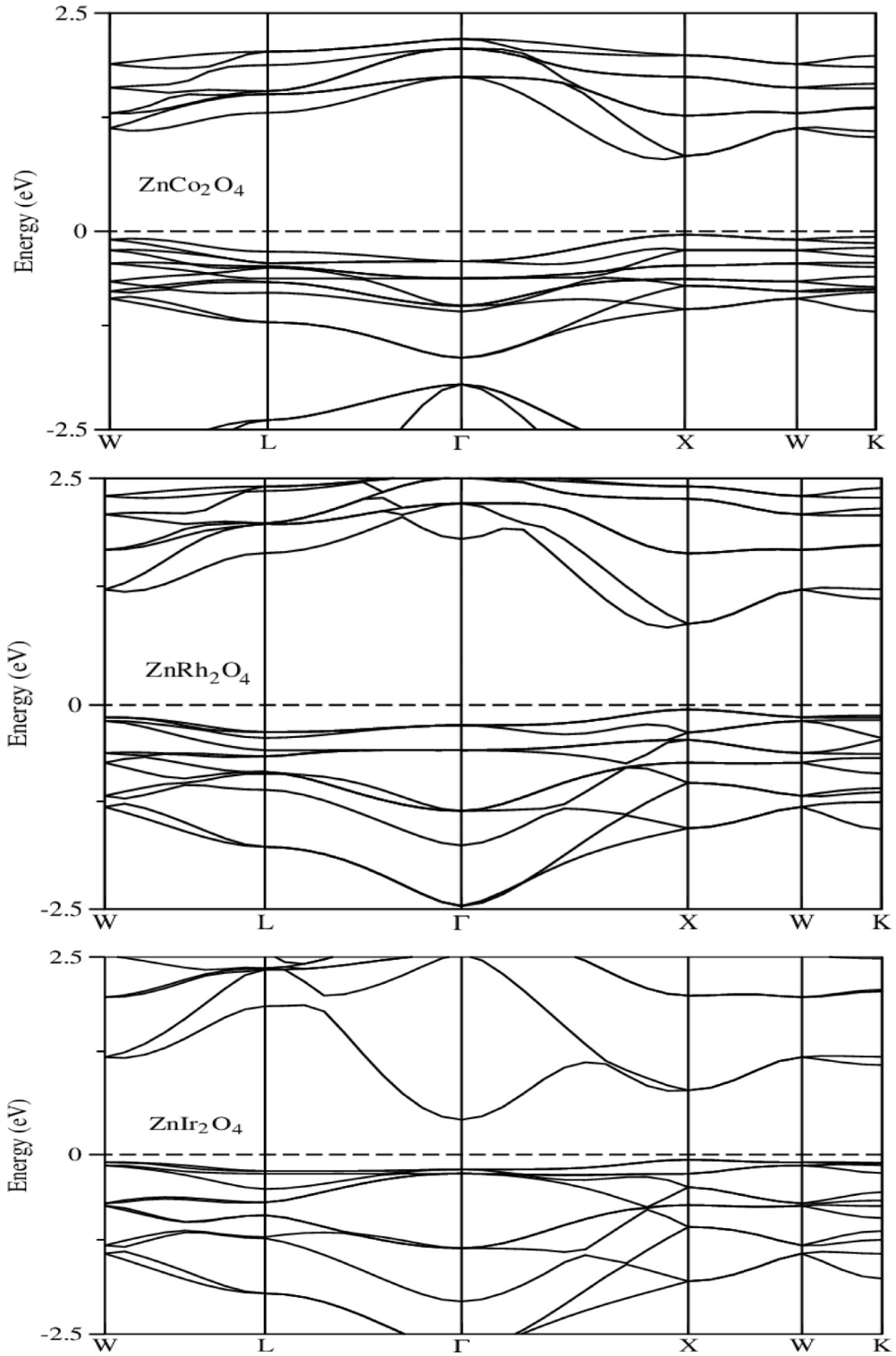

Fig. 2. The computed electronic band structure of cubic spinel ZnM_2O_4 (M = Co, Rh, Ir) compounds.

Poisson's ratios and elastic constants (C_{ij}) of spinel oxides ZnM_2O_4 (M = Co, Rh, Ir) are summarized in Table 2. According to the Born stability criteria [38], the computed values of the elastic constants is indicative of the mechanical stability of ZnM_2O_4 (M= Co, Rh, Ir) in the spinel structure.

Table 2
The computed values of direct band gaps (Γ − Γ, L − L, X − X) and indirect band gaps (Γ − L, Γ − X) for ZnM2O4 (M = Co, Rh, Ir) compounds.

Compounds	References	Γ − Γ	L − L	X − X	Γ − L	Γ − X
$ZnCo_2O_4$	This work	2.21	1.65	0.94	1.76	1.25
	[8-HSE]	–	–	–	–	3.88
	[13-Exp.]	–	–	–	–	2.26
	[16-Exp.]	–	–	–	–	2.63
	[24- PBE]	–	–	–	–	0.71
	[24-TB-mBJ]	–	–	–	–	3.36
	[24-HSE]	–	–	–	–	3.86
	[25-PBE]	–	–	–	–	0.773
	[25-TB-mBJ]	–	–	–	–	3.354
	[27-PBE]	–	–	–	–	0.57
	[27-HSE]	–	–	–	–	3.86
$ZnRh_2O_4$	This work	2.17	2.06	0.99	2.00	1.14
	[8-HSE]	–	–	–	–	2.91
	[9- PBE]	–	–	–	–	1.10
	[13-Exp.]	–	–	–	–	2.74
	[15]	–	–	–	–	1.2
	[18]	–	–	–	–	1.65
	[24- PBE]	–	–	–	–	0.89
	[24-TB-mBJ]	–	–	–	–	2.53
	[24-HSE]	–	–	–	–	2.87
	[25-PBE]	–	–	–	–	0.897
	[25-TB-mBJ]	–	–	–	–	2.53
	[27-PBE]	–	–	–	–	0.80
	[27-HSE]	–	–	–	–	2.87
	[29]	–	–	–	–	2.1
$ZnIr_2O_4$	This work	0.66	2.18	0.92	2.17	0.86
	[8-HSE]	–	–	–	–	2.53
	[11-B3LYP]	–	–	–	–	3.06
	[13-Exp.]	–	–	–	–	2.97
	[24- PBE]	–	–	–	–	0.28
	[24-TB-mBJ]	–	–	–	–	2.30
	[24-HSE]	–	–	–	–	2.45
	[25-PBE]	–	–	–	–	0.416
	[25-TB-mBJ]	–	–	–	–	2.32
	[27-PBE]	–	–	–	–	0.48
	[27-HSE]	–	–	–	–	2.45
	[28-LDA-mBJ]	–	–	–	–	2.25

$$(C_{11} - C_{12}) > 0,\ C_{12} < B < C_{11},\ (C_{11} + 2C_{12}) > 0,\ C_{44} > 0 \quad (1)$$

The elastic constant C_{11} represents the resistance in the x-direction against the linear compression. The elastic constants C_{11} of $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ compounds are larger than C_{12} and C_{44}, indicating that these compounds are less compressible along the x-direction. Unfortunately, no experimental or theoretical data are available for the elastic constants of these materials.

The B/G ratios for the three spinel oxides compounds were calculated. While materials with a B/G ratio of less than 1.75 exhibit brittle behaviour, materials with a B/G ratio greater than 1.75 exhibit ductile behaviour. The $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ compounds were shown to be ductile when their B/G ratio was greater than 1.75. Also, Cauchy pressure (C_{11}—C_{44}) are classical criteria that determine whether the material is ductile or brittle. The positive or negative value of the Cauchy's pressure indicates that the material is ductile or brittle. In this study Cauchy-pressure was found to be positive in the press, so the compounds studied were confirmed to be ductile in nature.

In addition, Young's modulus (E) and Poisson's ratio (ν) were calculated. The stiffness of the compounds was analysed by comparing the Young's modulus. The higher Young's modulus shows better stiffness, so $ZnCo_2O_4$ is the hardest compound in this work. The Poisson ratio was calculated between the elastic parameters to determine the types of forces in the materials. According to the Pugh criteria [39], if the Poisson ratio is around 0.1, the material has a covalent bond, if it is about 0.25, the material has an ionic bond [39]. In addition, the Poisson's ratio had a critical value of 0.26 indicating whether a material was ductile or brittle. The calculated ν values indicated that all materials were ductile.

3.4. Vibrational properties

The calculated full phonon dispersion curves, the total and projected density of states for spinel oxides ZnM_2O_4 (M = Co, Rh, Ir) compounds in the spinel structure along the high-symmetry directions are shown in Fig. 4. According to the symmetry analysis spinel ZnM_2O_4 (M = Co, Rh, Ir) compounds have 42 phonon modes, there are 39 optical modes distributed on the following symmetries at the Γ point.

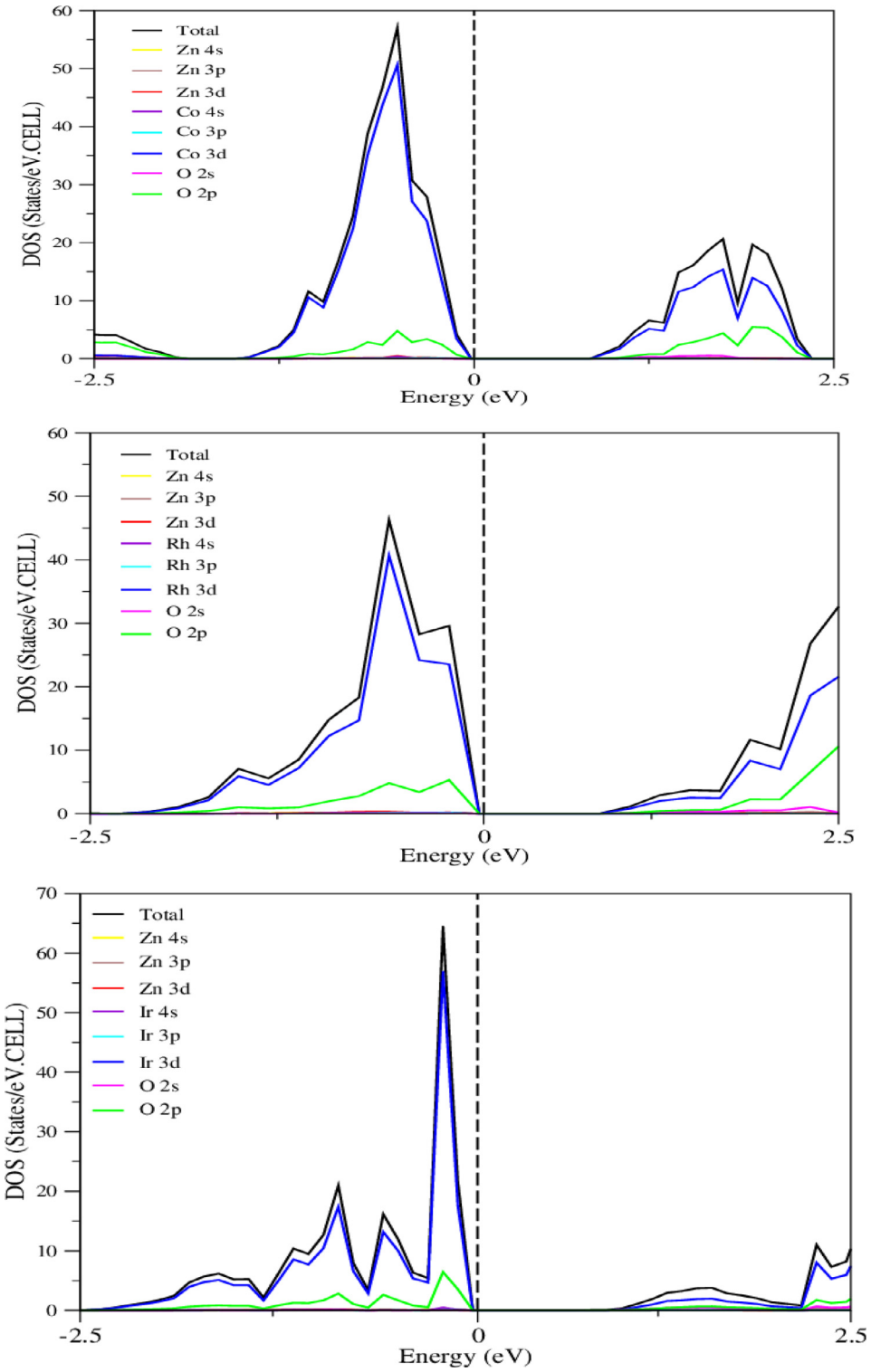

Fig. 3. The total and partial density of states for cubic spinel ZnM_2O_4 (M = Co, Rh, Ir) compounds.

$$\Gamma = A_{1g} + 2A_{2u} + E_g + 2E_u + T_{1g} + 4T_{1u} + 2T_{2u} + 3T_{2g} \quad (2)$$

where T_{1u} modes are infrared active, A_{1g}, E_g and T_{2g} modes are Raman actives and A_{2u}, E_u, T_{2u} and T_{1g} are silent (inactive). The phonon properties of ZnM_2O_4 (M = Co, Rh, Ir) compounds are calculated within the generalized gradient approximation (GGA) in

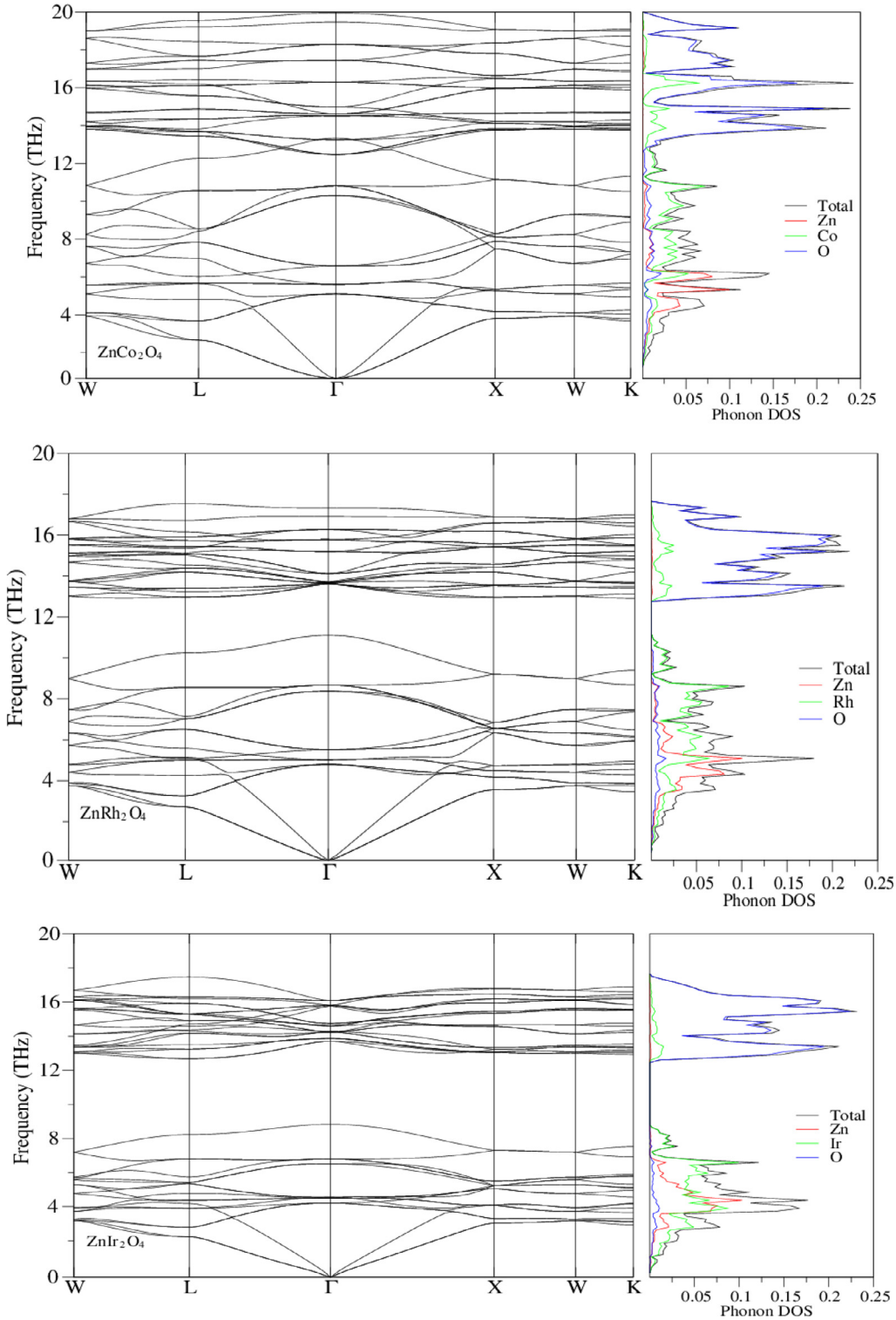

Fig. 4. Full phonon spectra and projected phonon density of states of cubic spinel ZnM_2O_4 (M = Co, Rh, Ir) compounds.

the spinel structure, with space group symmetry Fd-3 m (#227). From the phonon dispersion spectra, the band gap values were observed to be 3.85 THz and 1.84 THz for $ZnIr_2O_4$ and $ZnRh_2O_4$ compounds, respectively. $ZnRh_2O_4$ exhibits similar phonon dispersion properties with the same space group (Fm-3 m, (225)) materials such as Rh_2TiAl, Rh_2FeAl and $MgXH_3$ (X = Fe, Co) [40–42]. The calculated phonon dispersion curves of ZnM_2O_4 (M = Co, Rh, Ir) compounds confirm that three compounds are dynamically

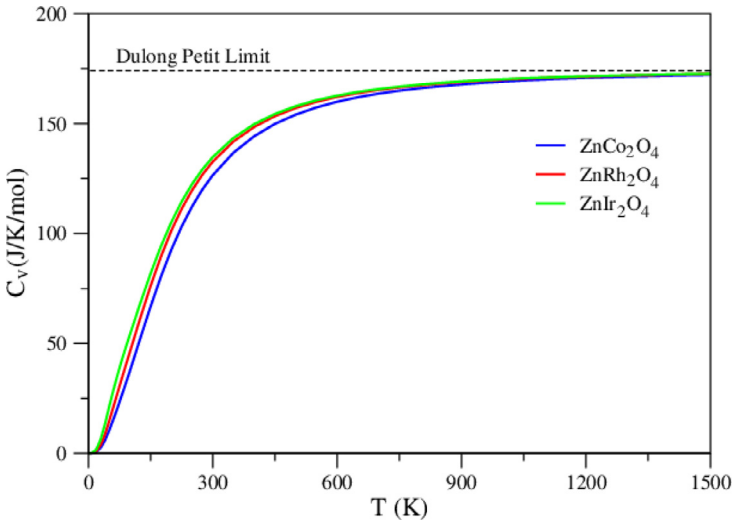

Fig. 5. Specific heats at constant volume versus temperature of cubic spinel ZnM_2O_4 (M = Co, Rh, Ir) compounds.

stable in the spinel structure without any imaginary phonon frequencies. The ZnM_2O_4 (M = Co, Rh, Ir) spinel compounds have not been compared with available data because there are no studies about their phonon frequencies.

4. Conclusion

In this study, the structural, elastic, electronic and phonon properties of ZnM_2O_4 (M = Co, Rh, Ir) in the spinel structure have been investigated using first principle density functional theory (DFT) within the generalized gradient approximation (GGA). The lattice constant (a_0), the internal parameter (u), Bulk modulus and elastic constants for ZnM_2O_4 (M = Co, Rh, Ir) are determined and evaluated. It can be seen that the $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ compounds show ductile manner and meets the well-known mechanical stability criteria for crystals. From the calculated electronic band spectra, we obtained indirect band gap values of 1.25 eV, 1.14 eV and 0.86 eV for $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ spinels, respectively. The phonon dispersion curves of $ZnCo_2O_4$, $ZnRh_2O_4$ and $ZnIr_2O_4$ spinel compounds along all symmetry directions in the Brillouin zone have been investigated for the first time in this work. From phonon dispersion curves, there is a gap between optical-optic phonon modes, except for the $ZnCo_2O_4$ spinel compound. This gap is caused by the mass difference between the atoms. It also shows that these alloys are dynamically stable because the phonon frequencies are not imaginary. Fig. 5 show the calculated the specific heat capacity (C_v) at a constant volume of spinel oxides ZnM_2O_4 (M = Co, Rh, Ir) compounds. The C_v values of these compounds increase rapidly in the 250 K range before starting the saturation point. At low temperatures, acoustic modes are important where optical modes take over at elevated temperatures due to electrostatic interactions. At a high-temperature, the calculated specific heat capacity C_v of these compounds are nearly to the Dulong-Petit limit [42,43]. Finally, using the computed phonon density of state, the specific heats (C_v) at constant volume has been determined using by the quasi harmonic approximation (QHA).

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