DFT Studies on Optical Properties of Half Heusler Alloys XCaB (X=Li,Na,K)

A disseration submitted to the Department of Physics, Dibrugarh University for the partial fulfillment of the requirements for the award of the degree of Masters of Science in Physics

by

Deepshikha Burman

IMSc in Physics, 10th Semester

Roll No: 17202002

Under the guidance of

Dr. Bulumoni Kalita

Assistant Professor

Department of Physics

Dibrugarh University

August, 2022

CERTIFICATE

This is to certify that the project report submitted by Deepshikha Burman, Roll No:17202002, IMSc 10th semester, in Department of Physics, has prepared the project report entitled:

"A DFT Study on Optical Properties of Half-Heusler compounds XCaB(X=Li,Na,Ca)".

This project is carried out under the guidance and supervision of Dr.Bulumoni Kalita . The sources of literature of information derived from the existing literature has been indicated throughout the report at appropriate places.

The project report embodies original work and has not been copied from any other sources.

(Signature)

Dr. Bulumoni Kalita

Assistant Professor

Department of Physics

Dibrugarh University

Dibrugarh

(Signature)

Dr. Prasanta Kumar Saikia

Head of the Department

Department of Physics

Dibrugarh University

Dibrugarh

DECLARATION

I hereby declare that the project report entitled: "A DFT Study on Optical Properties of Half-Heusler compounds XCaB(X=Li,Na,Ca)", submitted to the Department of Physics, Dibrugarh University is an original work out by me under the guidance and supervision of Dr. Bulumoni Kalita Ma'am, Assistant Professor, Department of Physics, Dibrugarh University. The source of literature of information derived from the existing literature has been indicated throughout the report at appropriate places.

Deepshikha Burman

Deepshikha Burman

Roll No: 17202002

Registration No:17991038

IMSc 10th semester

Department of Physics

Dibrugarh University

2

ACKNOWLEDGEMENT

At the very onset it gives me immense pleasure and satisfaction to remember those persons who helped me to a large extent in accomplishing my project work. I would like to express my heartful gratitude to my supervisor, Dr. Bulumoni Kalita Ma'am, for giving me the oppurtunity to work under her guidance and for providing the necessary infrastructure and facilities needed for the completion for the work. I am thankful to her for her untiring patience, motivation, enthusiasm and immense knowledge and for providing academic, technical and moral support in my study and research.

I would also like to thank our Head of the Department, Dr. P.K Saikia Sir for including the subject in our course. I would like to thank research scholars Rituparna Hazarika, Bishwajit Boruah, Geetimallika Das and Saujanya Adhyapak for helping to complete my project. Finally, I would like to thank my family and friends, including my partner Hirashree Pathak, for helping me and supporting me.

I have tried my utmost to bring up the project vividly. If any error is noted, please consider.

<div align="right">

Deepshikha Burman

Roll No: 17202002

Registration No:17991038

IMSc 10th semester

Department of Physics

Dibrugarh University

</div>

Contents

List of Figures

List of Tables

Abstract

We have studied for the first time the optical properties of half Heusler compounds $XCaB$ ($X = Li, Na, Ca$) using density functional theory (DFT) in our dissertation work. Moreover, the effect of application of tensile and compressive strains on the optical properties have also been investigated. The results obtained from these investigations are presented in the present dissertation report. The report specifically describes how strain of different types and strengths influences the optical behaviours such as dielectric function, refractive index, absorption coefficient and reflectivity of the considered alloys. Our observations are correlated with the electronic structure calculations performed by Ms. Hirashri Pathak for her dissertation work in M. Sc. 4th Semester, Department of Physics, Dibrugarh University, 2022.

Chapter 1

Introduction

Heusler alloy is an exciting class of multifunctional alloy discovered by Fredrich Heusler, in the year 1903. In his study, he discovered that Cu_2MnAl type alloy behaves like ferromagnets, although none of its constituents are magnetic in nature [1]. These type of alloys have chemical composition of the form X_2YZ and are named as full-Heusler (FH) alloy with stoichiometric ratio 2: 1: 1 where X, Y are typically transition metals and Z is the main p-block element [1]. These FH alloys are found to exhibit a special property known as half-metallicity, where one spin channel is metallic while the other is semiconducting in nature leading to 100% spin polarization near the fermi level [2, 3]. Another interesting class of compound, named as half-Heusler(HH) alloy whose structure and composition is similar to full-Heusler alloy except that one X atom is removed from X_2YZ leaving a vacant site [23]. Thus, HH alloy has an elemental composition XYZ with stoichiometric ratio 1:1:1. Here X belongs to S block/transition metal/Rare earth elements, Y can be both transition or non-transition metal and Z belongs to main group element (P- block) [1]. The most electropositive element is placed at the beginning of the formula and electronegative element is placed at the end of the formula [1]. The structure of half-Heusler alloy can be described as an interconnection between Rock salt (NaCl) and Zinc blende (ZnS) structure. They are termed as filled tetrahedral structures as these ternary compounds are formed by filling the vacant

lattice sites of binary lattice [1]. They crystallizes in a non-centrosymmetric cubic structure with space group no. 216, F-43m, $C1_b$ [1]. The structure is made up of 3 inter – penetrating FCC sub lattice with the Wyckoff positions of X,Y and Z as, $r_1 = A(0.5, 0.5, 0.5)$, $r_2 = B(0, 0, 0)$ and $r_3 = C(0.25, 0.25, 0.25)$ respectively. By interchanging the atoms at r_1 and r_2, three phases α, β and γ are formed. i.e., X, Y and Z atoms are arranged at different positions (r_1, r_2, r_3), (r_3, r_1, r_2) and (r_2, r_3, r_1) respectively [2].
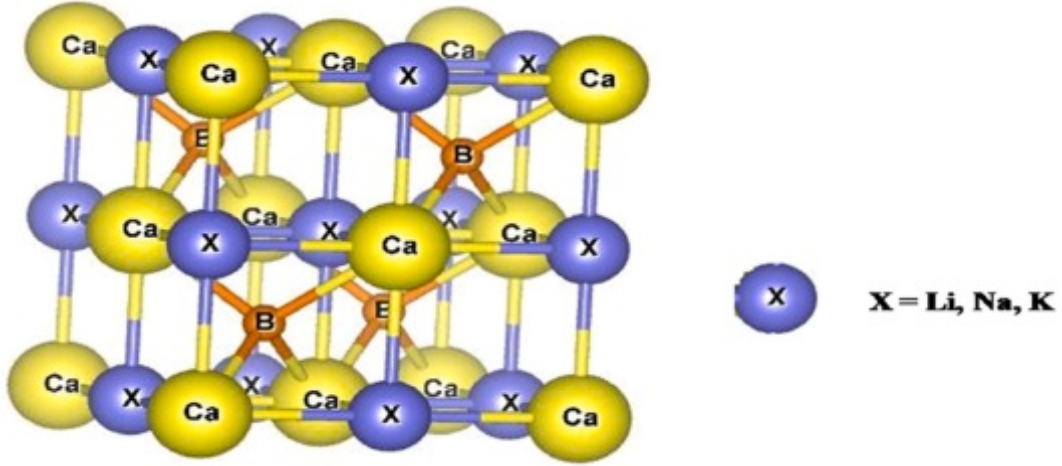
Figure 1.1: Crystal structure of XCaB (X= Li,Na and K)

For the first time, Groot *et.al.* predicted that HH alloys also exhibit half-metallic behaviour by studying the band structure of Mn based HH alloys, NiMnSb and PtMnSb and since then half-Heusler alloys has been studied widely [5]. HH alloys on the other hand can be semiconducting as well as half-metallic ferromagnet depending on the valence electron count of the alloy (VEC). This concept was first introduced by Pierre *et.al* and suggested that the electronic properties of HH alloys depend on the VEC of the compound [23]. HH compounds with VEC 8 and 18 are diamagnetic semiconductors while others are half metallic ferromagnets [6]. 8 VEC compounds are also called as semi-Heusler or Juza-Nowotny compounds with a wide band gap [3, 6]. These alloys have gained much attention in the last few decades due to its simple crystalline structure, tunable band gaps, flexible com-

position, excellent mechanical strength and high thermal stability [7]. Moreover they are non-toxic in nature, easily available, highly durable, environment friendly and more cost effective [22]. HH alloys are considered to be potential candidate for various applications such as spintronics [2], topological insulators [9, 10], thermoelectric materials [11, 12] and optoelectronic devices[13, 24, 15, 16]. Thus, HH alloy were investigated both theoretically and experimentally, where the electronic, magnetic, spintronics, thermoelectric properties as well as optical properties were discussed. Dhakshayani et $al.$ studied the electronic, magnetic and thermoelectric properties of $XCaB$ ($X = Li, K, Na, Rb$) alloy. They discussed that the alloy is ferromagnetic in nature i.e. the up spin or the majority channel shows semiconducting behaviour while the down spin shows metallic behaviour thus exhibiting half metallic character which is applicable for spintronics [16]. Umamaheswari et $al.$ also studied the half metallic ferromagnetism property of half –heusler compounds XYZ ($X = Li, Na, K$ and Rb; $Y = Mg, Ca, Sr$ and Ba; $Z = B, Al$ and Ga) in all three phases and found that alpha phase is the most stable among the three [3]. Azouaoui et $al.$ mainly studied the thermoelectric and optical property of the alloy $LiCaX$ ($X = N, P$ and As) along with the structural and electronic properties of the alloy. The calculated electronic properties showed that all the considered HH alloys are semiconducting (8 VEC) with indirect band gap [6]. Kieven et $al.$ studied eight VEC half-Heusler compounds in order to find suitable semiconductors for optoelectronics such as Cd-free buffer layer materials for chalcopyrite-based thin-film solar-cell devices [13]. H. Joshi et $al.$ reported the elastic and optical properties of half-Heusler compounds $MCoSb$ ($M = Ti, Zr$ and Hf). This study reveals that the optical properties depend on the semiconducting nature of the alloy [24]. Saeidi $et.al.$ studied another class of HH alloys $RnMnZ(Z = P, As)$ that exhibit half metallic behaviour and are found to be optically metallic. They extensively studied the effect of intraband transition of the compounds inspired by

Mehmood *et.al* [16] as they worked on the same compound without considering intraband transition. They revealed the importance of intraband transition in the optical properties of half metals at low energy range [15].

It is interesting that the HH alloys get largely affected by the application of strain and by tuning the electronic properties thermoelectric efficiency can be increased. Nisha *et.al* have studied the application of isotropic strain on the compound $TaIrGe$ to increase its thermoelectric efficiency. They found that, by tuning the the electronic band structure of the compound, the transport property enhances [11]. Recently, Anuradha Saini *et al.* studied the effect of isotropic strain (tensile and compressive) on the electronic structure, elastic properties and transport properties of $LiScGe$ alloy. They found that $LiScGe$ is an indirect band gap semiconductor under isotropic strain. The value of ZT increases due to increase in both tensile strain for n-type $LiScGe$ and compressive strain for p-type $LiScGe$ [17].

Chapter 2

Motivation

It is known that electronic structure plays an important role in determining the optical behaviour of a material. The magnitude and nature of band gap describes how the material reacts to incident light. There are two basic transition processes. They are interband and intraband transitions. When electronic transition takes place between valence band and conduction band, it is called interband transition. On the other hand, in the ground state of a material, if the incident radiation has energy less than the band gap, then electronic transitions may occur within the valence band itself resulting in intraband transition.

Half Heusler alloys with valence electron count (VEC) value of 8 and 18 are found to be semiconducting, whereas the others are half-metallic ferromagnetic in nature [23]. Very recently, Dhakshayani *et al.* have studied a group of 6 VEC compounds with compositions $XCaB$ ($X = Li, Na, K$ and Rb) and showed their thermoelectric properties [12]. It has been found in this study that the thermoelectric response of the mentioned compounds depend on their semiconducting states. However, the effect of strain on these properties has not been studied. A. Sainia *et al.* studied the effect of isotropic strain on transport properties on a compound $LiScGe$ [17]. Azouaoui *et al.* have studied a similar group of HH compounds, $LiCaZ$ ($Z = N, P$ and As) for optoelectronic applications [6]. Saeidi *et. al.* observed that intraband

transition has the main role in optical properties of half metallic Heusler alloys at low energy ranges $(0 - 1$ eV$)$ [15]. In another study, N. Mehmood *et. al.* showed that the half Heusler alloys $RnMnZ$ $(Z = P, As)$ are optically metallic [11]. For these half metallic materials, metallic (majority spin) nature was found to be more significant than the semiconducting state (minority spin).

In spite of the available literatures on electronic and optical properties of the HH alloy as discussed above, optical properties of $XCaB$ $(X = Li, Na, K)$ alloys are still missing to the best of our knowledge. Moreover, the study of the effect of strain on the optical properties of these materials will also be interesting. Therefore in the present work, we aim to investigate the optical properties of both unstrained and isotropically strained compounds of $XCaB$ $(X = Li, Na$ and $K)$. We will consider the isotropic strain of tensile and copressive natures in the range of $\pm 10\%$.

Chapter 3

Methodology

The spin polarised calculations have been performed through density functional theory (DFT) approach implemented in the Quantum Espresso 5.2.0 package [21]. The interaction between ions and electrons are described by Optimized Norm-Conserving Vanderbilt (ONCV) pseudopotentials [22]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) is used as exchange-corelation functional [23]. An energy cut-off value of 60 Ry and $6 \times 6 \times 6$ Monkhorst-Pack k-point grid [24], achieved by convergence test, was set for explaining the plane wave expansion of the electronic wave function and Brillouin zone sampling of the system, respectively. A dense k-mesh grid $30 \times 30 \times 30$ is used to study the electronic properties. All the geometric coordinates of the structures are optimised till the threshold of total energy $(10^{-4}Ry)$ and force $(10^{-3}Ry/Bohr)$ are reached. Gaussian smearing of a width of $0.002Ry$ is employed to improve convergence.

For performing our calculation we have used self consistent field procedure which is an iterative method. A corresponding input file for scf calculation is shown below.

```
&control
    calculation = 'scf',
    prefix = 'LiCaB_oncv_optics'
    outdir = '/home/bulumoni/Desktop/Msc_4th_sem_Project_2022/Hirashri/conv/temp/'
    pseudo_dir = '/home/bulumoni/Research_new/MPhil/Rituparna/Espresso_practice/pseudo/'
    verbosity = 'high'
/
&system
    ibrav =  2,
    celldm(1) = 11.7742,
    nat =  3,
    ntyp = 3,
    ecutwfc = 60,
    nbnd = 20,
    occupations = 'smearing',
    smearing = 'gaussian',
    degauss = 0.002,
    nspin =2
    starting_magnetization(1) = 0.5
    starting_magnetization(2) = 0.5
    starting_magnetization(3) = 0.5

/
&electrons
    mixing_beta = 0.7
/
ATOMIC_SPECIES
 Li 6.941 Li.upf
 Ca 40.078 Ca.upf
 B 10.811 B.upf

ATOMIC_POSITIONS (alat)
 B  0.25 0.25 0.25
 Ca 0.00 0.00 0.00
 Li  0.50 0.50 0.50
```

3.1 Optical Properties

Interaction of light with matter gives rise to different phenomenon such as absorption, reflection, refraction, diffraction, scattering, transmission etc. Optical behaviours vary with composition and dimension of materials along with various external factors such as temperature, pressure etc. In order to study and estimate the optical response of material, we define several optical parameters, namely refractive index, polarisability, absorption coefficient, reflectivity, transmissivity, etc. Dielectric function, a measure of the change in electronic charge distribution in a material caused by the application of an external electric field, basically governs the optical properties of the material. It is denoted by the the symbol ϵ, which is a function of incident wave frequency ω. It is complex in nature i.e, it has a real

(ϵ_1) and an imaginary part (ϵ_2).

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$$

To investigate the optical properties of the hH alloys, random phase approximation (RPA) method incorporated in Epsilon.x code is used [23, 24]. In this approximation, the imaginary part of the dielectric function is calculated using the expression,

$$\epsilon_2(\omega) = \frac{2\pi e^2}{\Omega\epsilon_0} \sum_{k,v,c} | < \Psi_k^c|\widehat{u}.r|\Psi_k^v > |\delta[E_k^c - E_k^v - E] \tag{3.1}$$

where,

$\omega \rightarrow$ frequency of the incident light

$k \rightarrow$ reciprocal space points

$\Omega \rightarrow$ volume of the primitive cell

c and $v \rightarrow$ conduction and valence band

Using the Kramer-Kronig's relations the real part of the dielectric function is determined by following formula,

$$\epsilon_1 = 1 + \frac{2}{\pi}P \int \frac{\omega'\epsilon_2(\omega')}{\omega'^2 - \omega^2} \tag{3.2}$$

$P \rightarrow$ principal value of the integral

The real and imaginary part of dielctric function is utilised to calculate the optical parameters such as refractive index, extinction coefficient, absorbtion coefficient and reflectivity .

9

Refractive index (n) which describes how fast the light can travel through a medium is calculated by using the following relation,

$$n = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1}{2}} \qquad (3.3)$$

The extinction coeffiecient (k) which measures the attenuation of the light wave when passed through a medium is calculated using the relation,

$$k = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1}{2}} \qquad (3.4)$$

Reflectivity (R) and absorption coefficient (α) are calculated using equations 3.5 and 3.6, respectively.

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \qquad (3.5)$$

$$\alpha = 4\pi \frac{k}{\lambda} \qquad (3.6)$$

The input file to obtain the real and imaginary part of the dielectric function is shown below.

```
&inputpp
    calculation = 'eps',
    prefix = 'LiCaB_oncv_optics'
    outdir = '/home/bulumoni/Desktop/Msc_4th_sem_Project_2022/Hirashri/conv/temp/'
/
&energy_grid
    smeartype = 'gauss'
    intersmear = 0.136d0
    intrasmear = 0.136d0
    wmax = 30.0d0
    wmin = 0.0d0
    nw = 600
    shift = 0.0d0
/
```

3.2 Strain

Strain is the ratio of amount of deformation experienced by the material in the direction of force applied to the initial dimensions of the material. There are two main types of strain: tensile and compressive. Fractional increase in the dimensions of the material is called tensile strain (denoted by '+' sign), whereas fractional decrease is called compressive strain (denoted by '-' sign).

To investigate the effect of strain on the optical properties of the considered compounds, we have applied both tensile (5% and 10%) and compressive (-5% and -10%) strains isotropically. The simulations of both tensile strain and compressive strain are done by increasing and decreasing the lattice parameter of unstrained compounds (a_0), respectively, which is represented as [22],

$$\triangle a = a - a_0$$

where,

$a_0 \rightarrow$ the lattice parameter of the unstrained compound

$a \rightarrow$ the lattice parameter of the strained compound

Hence, the compressive and tensile strain is represented by $\frac{\triangle a}{a_0} < 0$ and $\frac{\triangle a}{a_0} > 0$, respectively .

The input file for the calculation of LiCaB with 5% tensile strain is shown below.

```
&control
    calculation = 'scf',
    prefix = 'LiCaB_5p_ts'
    outdir = '/home/bulumoni/Desktop/Msc_4th_sem_Project_2022/Hirashri/conv/temp/'
    pseudo_dir = '/home/bulumoni/Research_new/MPhil/Rituparna/Espresso_practice/pseudo/'
    verbosity = 'high'
/
&system
    ibrav =  2,
    celldm(1) = 12.36291,
    nat =  3,
    ntyp = 3,
    ecutwfc = 60,
    nbnd = 20,
    occupations = 'smearing',
    smearing = 'gaussian',
    degauss = 0.002,
    nspin =2
    starting_magnetization(1) = 0.5
    starting_magnetization(2) = 0.5
    starting_magnetization(3) = 0.5

/
&electrons
    mixing_beta = 0.7
/
ATOMIC_SPECIES
 Li 6.941 Li.upf
 Ca 40.078 Ca.upf
 B 10.811 B.upf

ATOMIC_POSITIONS (alat)
 B  0.25 0.25 0.25
 Ca 0.00 0.00 0.00
```

Chapter 4

Results and Discussion

In this chapter, we will discuss the various optical properties as well as the effect of isotrpic strain on these properties of XCaB (X= Li, Na and K) compounds. The computed electronic properties of the considered alloys with and without strain suggest that these materials are of half metallic nature [22, 11, 20]. They have semiconducting electronic structure in the spin up state, whereas the spin down state is metallic. The energy band gap values corresponding to the semiconducting state [20] are shown in the Figure 4.1. In the following sections, we will present the computed results of dielectric function, absorption coefficient and reflectivity of the considered half Heusler alloys.
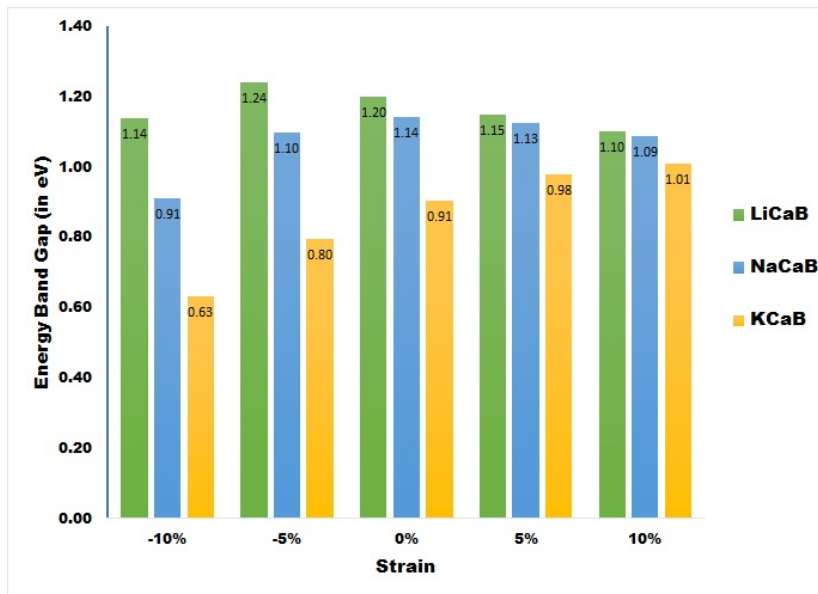

Figure 4.1: The variation of energy band gap with tensile and compressive strain in case of majority spin channel (semiconducting channel) [25].

4.1 Dielectric Function

Dielectric function provides information regarding the polarisation of the material due to presence of an external electric field. This external electric field is usually from the electromagnetic radiation striking the material. The polarisation explains whether the material is likely to undergo reflection, refraction, absorption or mixture of all or some of these phenomena.

The real part of the dielectric function (ϵ_1) for XCaB (X=Li, Na, K) alloys are shown in Figures 4.2(a)-4.2(c). The static dielectric constant values (ϵ_1 values in zero energy limit) in majority spin channel are found to be positive for all the compounds in both strained and unstrained cases. On the other hand, very large values of ϵ_1 (both positive and negative) are observed in lower energy ranges of minority spin channel (Figures 4.2(d)-4.2(f)). Similar behaviour of dielectric constant has also been previously observed for semiconducting and metallic states [24]. Moreover, we come to know from the electronic structure study [20] that for the considered compounds, majority and minority spin states are of metallic and semiconducting natures. Therefore, our computed results for real dielectric function are in agreement with the available information for the same.

Next, due to application of strain, we see deviations in the static dielectric constant values from that of the pristine structure (Table 4.1). Further, we have observed slight red shift in ϵ_1 for NaCaB and KCaB under application of tensile strain, whereas insignificant blue shift is observed under the application of compressive strain. On the other hand, no such distinct shift is noticed in case of LiCaB. In addition, the oscillatory behaviour of the real dielectric function (Figures 4.2(a)-4.2(c)) decreases with increasing energy for all the HH alloys. The height of the peaks for this parameter suggests the maximum polarisation occuring in the lower energies, ranging from IR to near UV region.
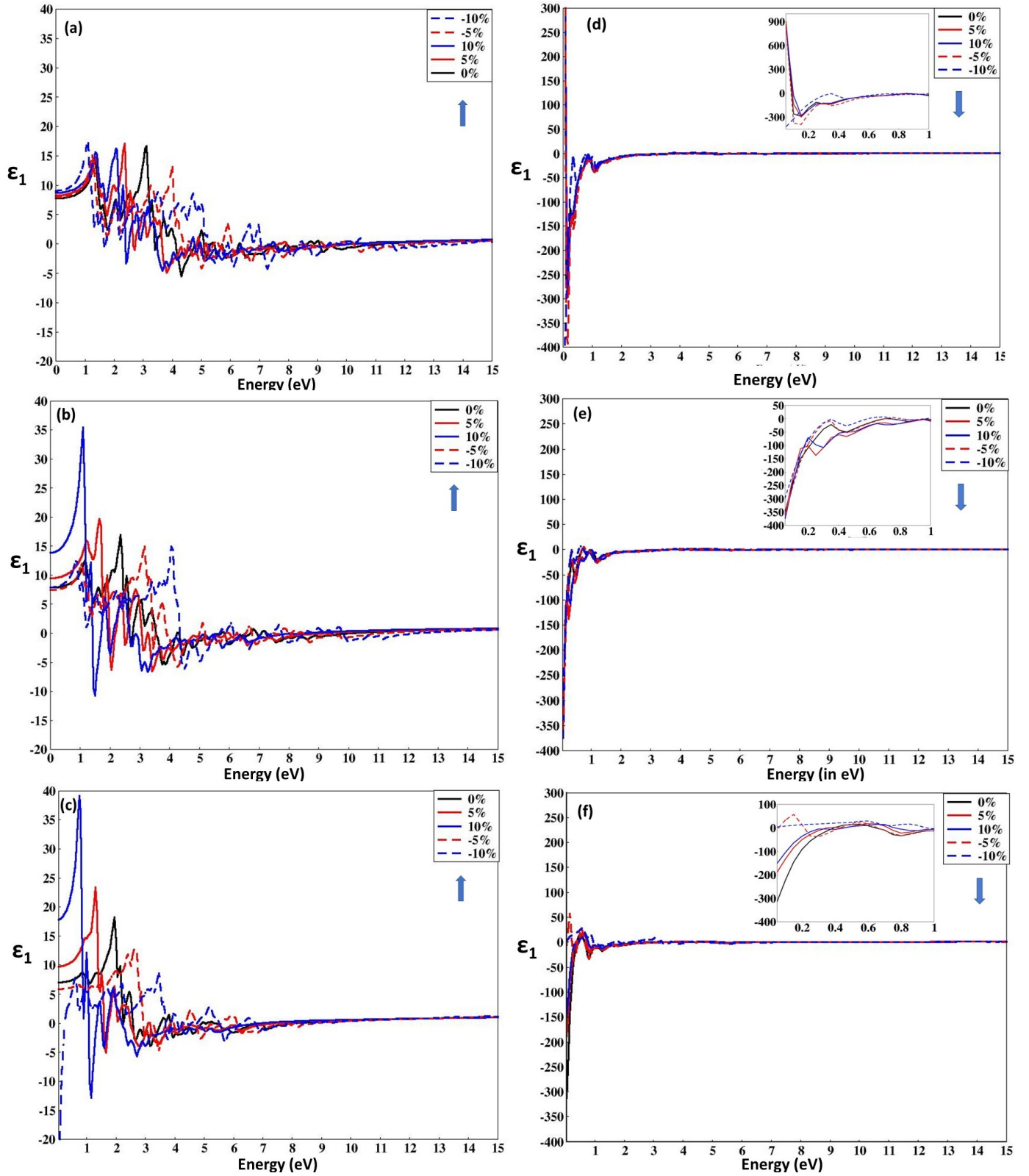
Figure 4.2: Real part of the dielectric function (ϵ_1) in majority spin state for a) LiCaB, b) NaCaB and c) KCaB; in minority spin state for d) LiCaB, e) NaCaB and f) KCaB
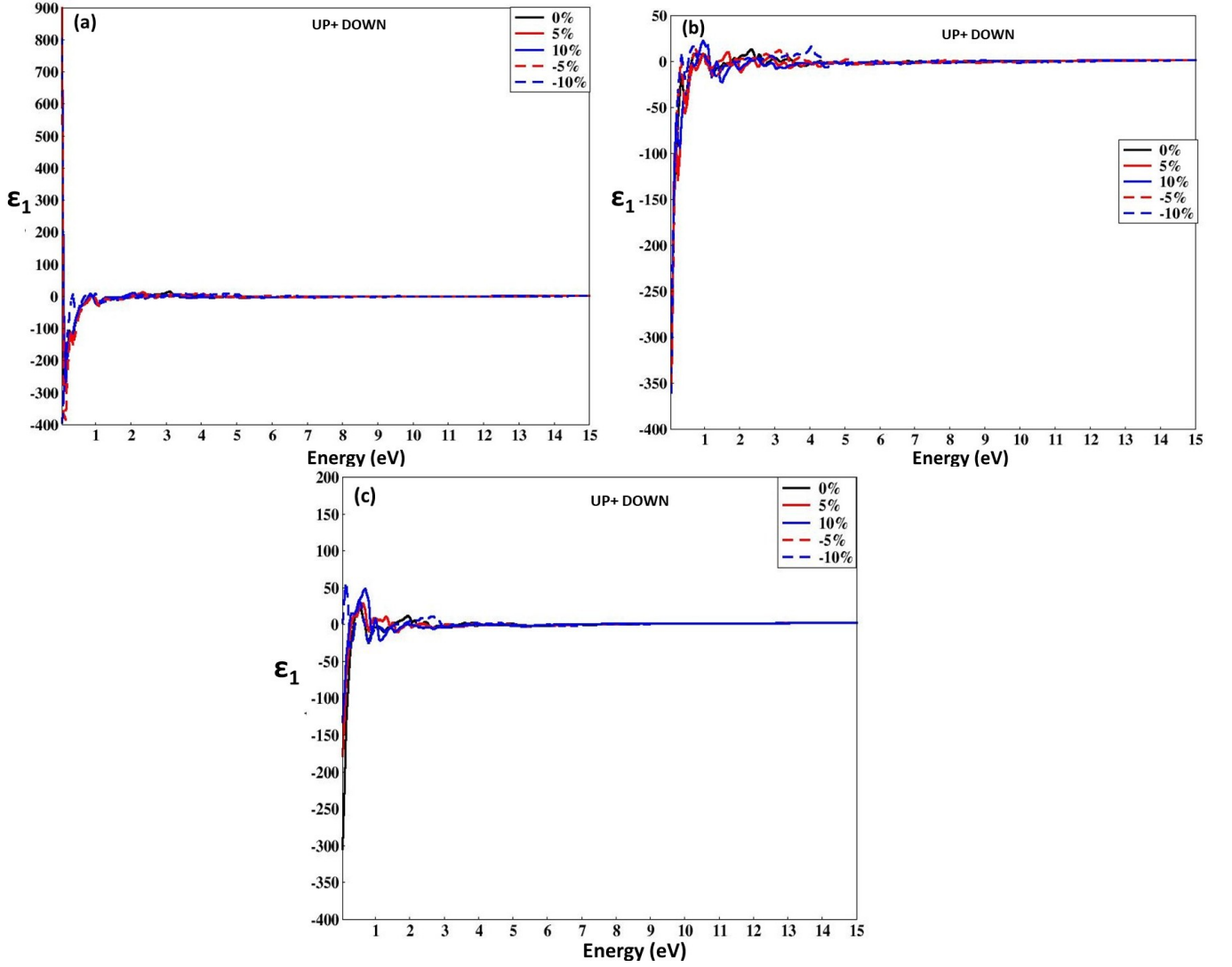
Figure 4.3: Real part of dielectric function for total spin a) LiCaB, b) NaCaB and c) KCaB.

The minority spin channel, which remain metallic (Figures 4.2(d)-4.2(f)) for the three compounds portrays unalteration under isotropic strain. Here, the intraband transition plays a prominent role in the lower energy ranges. Thus, in the IR region, we observe significant non-zero values of real dielectric function, which later on vanishes around the visible range. The behaviour of ϵ_1 in the minority spin state is unaffected due to the presence of strain. Another important feature is that the real dielectric function for total spin state is similar to that of the minority channel, suggesting dominating metallic behaviour on the optical properties of the compound.
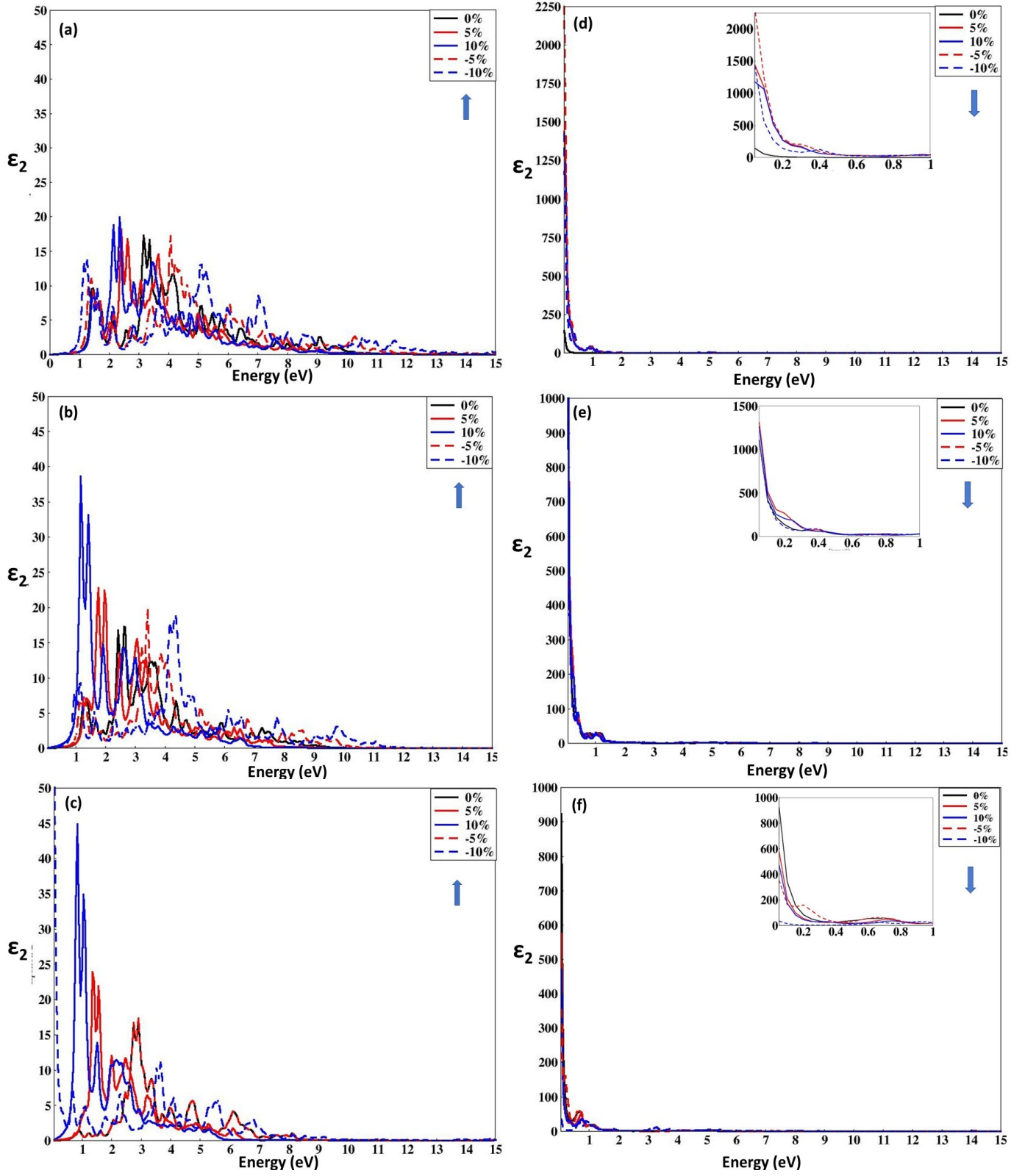
Figure 4.4: Imaginary part of the dielectric function (ϵ_1) in majority spin state for a) LiCaB, b) NaCaB and c) KCaB; in minority spin state for d) LiCaB, e) NaCaB and f) KCaB
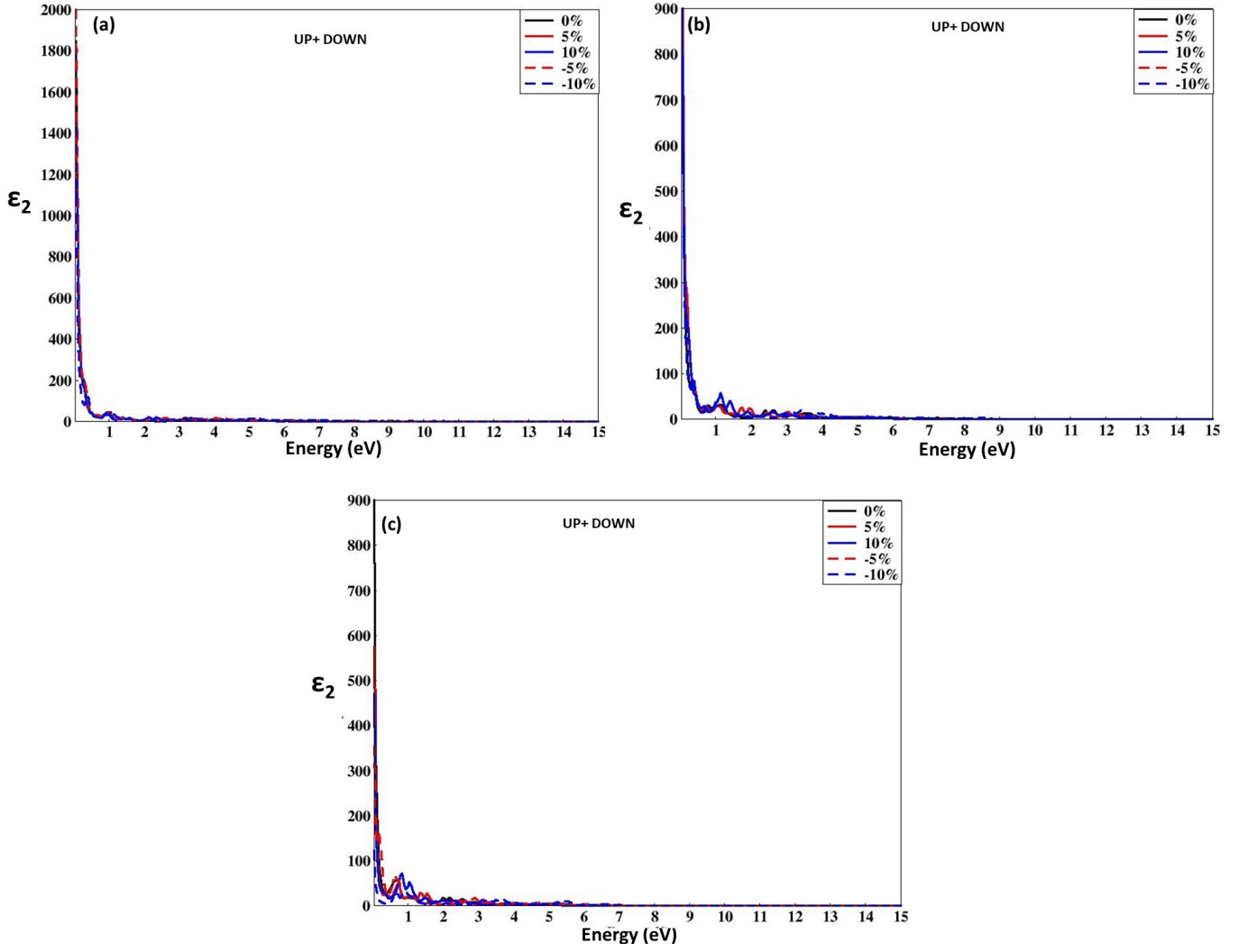
Figure 4.5: Imaginary part of dielectric function for total spin a) LiCaB, b) NaCaB and c) KCaB.

Table 4.1: The important optical parameters of HH alloys obtained from dielectric function curve of majority spin channel (semiconducting channel).

Compound	Strain	Static Dielectric Constant from ϵ_1
LiCaB	-10%	9.07
	-5%	7.94
	0%	7.74
	5%	8.26
	10%	8.69
NaCaB	-10%	7.91
	-5%	7.41
	0%	7.82
	5%	9.42
	10%	13.84
KCaB	-10%	-24.8
	-5%	5.83
	0%	7.04
	5%	9.73
	10%	17.79

The imaginary part of the dielectric function provides a picture of the electronic structure along with the nature of transitions giving rise to the phenomenon of optical absorption. From Figures 4.4(a - c), it is observed that the threshold values of the imaginary part of the dielectric function in the semiconducting states for XCaB (X=Li, Na, K) undergoes shift towards lower energies in going from LiCaB to KCaB. The behaviour of ϵ_2 in the minority spin channel signifies the existence of intraband transition at low energy IR region, which is consistent with observation of ϵ_1. For all the compounds, summing up the majority and minority spin states for both the real and imaginary parts of the dielectric function results in similar fashion as that of the individual minority channel. This observation clearly indicates that the optical properties of the considered alloys are governed by their metallic nature only without any dependence on their semiconducting states. It is important to mention here that the metallic state of the mentioned compounds are not affected by strain of different types and strenghts within the limit of $\pm 10\%$.

Both interband and intraband transition are considered in all the compounds, in the project. For the metallic channel, in every compound, it has been observed that intraband transitions has a significant role in the energy spectrum in the region 0-2eV, i.e at very low energy (from IR to visible range). While for the semiconducting channel, it has been observed from the calculations that, intraband transition does not have any significant influence. In most cases, it is found to be zero throughout the energy ranges. Saeidi $et.al$ [15] explained the importance of intraband transition in optical characterisation of HH alloys. They tried to explain how intraband transitions can be clearly shown if we observe the imaginary part of the dielectric function. They stated that, low energy photons transmit electrons inside metallic bands (i.e, intraband transitions occur) and when the incident energy is increased, the interband transition is experienced . These results have been verified in our

present work.

4.2 Absorption Coefficient and Reflectivity

The absorption coefficient $\alpha(\omega)$ of a material represents the fraction of incident electromagnetic radiation absorbed by unit thickness of that material. Values of absorption coefficient indicates the absorption behaviour of a material in different incident energy ranges. Reflectivity is another important parameter in optical characterisation that describes how a material behaves towards incident electronic radiation. Higher the value of reflectivity, lower is the tendency of a material to absorb incident radiation. Value of reflectivity is lower than unity.

We have computed the absorption coefficient and reflectivity of XCaB (X=Li, Na, K) alloys without and with isotropic strains. The calculations have been performed for both spin up and spin down states. It has been observed that the corresponding results in the total spin (spin up+spin down) state is exactly similar to that of the spin down (metallic) state. Therefore, we have shown the absorption coefficient and reflectivity plots only for spin up (Figures 4.6-4.8)) and total spin (Figures 4.9-4.11) states.
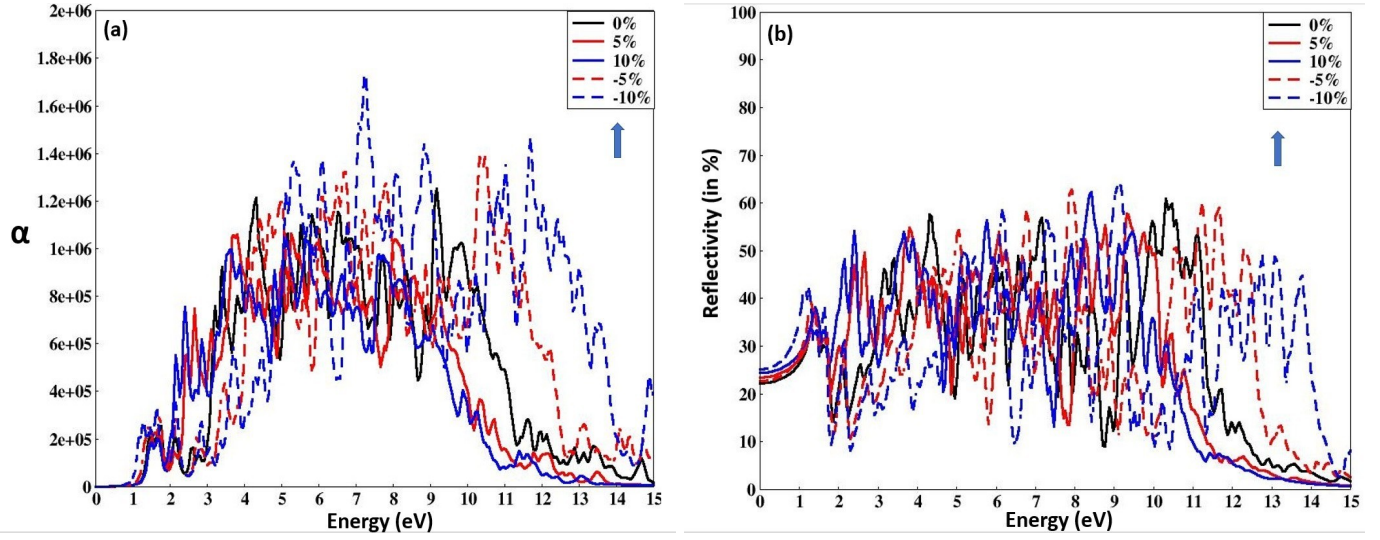
Figure 4.6: a) Absorption Coefficient (in cm^{-1}) and b) Reflectivity (%) for majority spin channel of LiCaB compound.
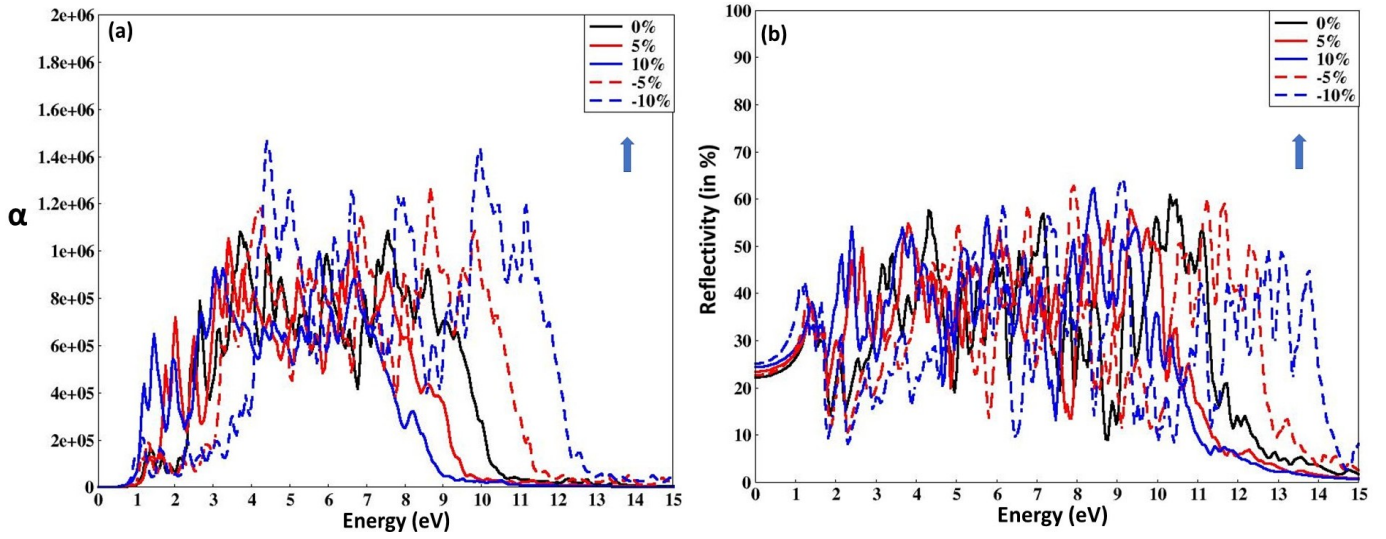

Figure 4.7: a) Absorption Coefficient (in cm^{-1}) and b) Reflectivity (%) for majority spin channel of NaCaB compound.
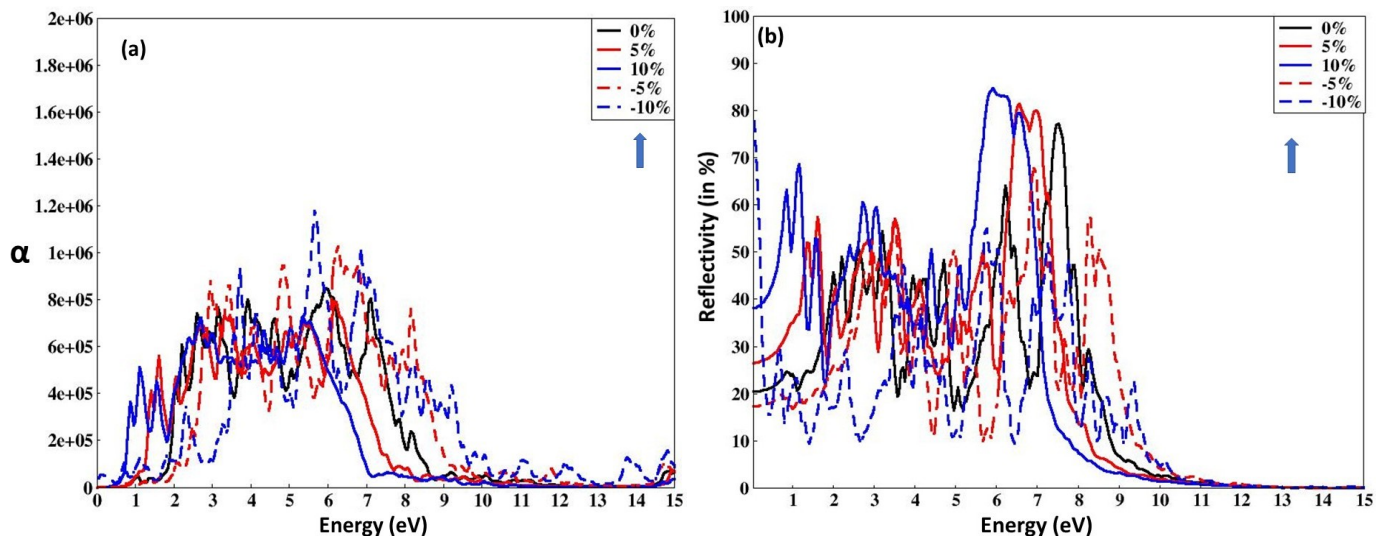

Figure 4.8: a) Absorption Coefficient (in cm^{-1}) and b) Reflectivity (in %) for majority spin channel of KCaB compound.
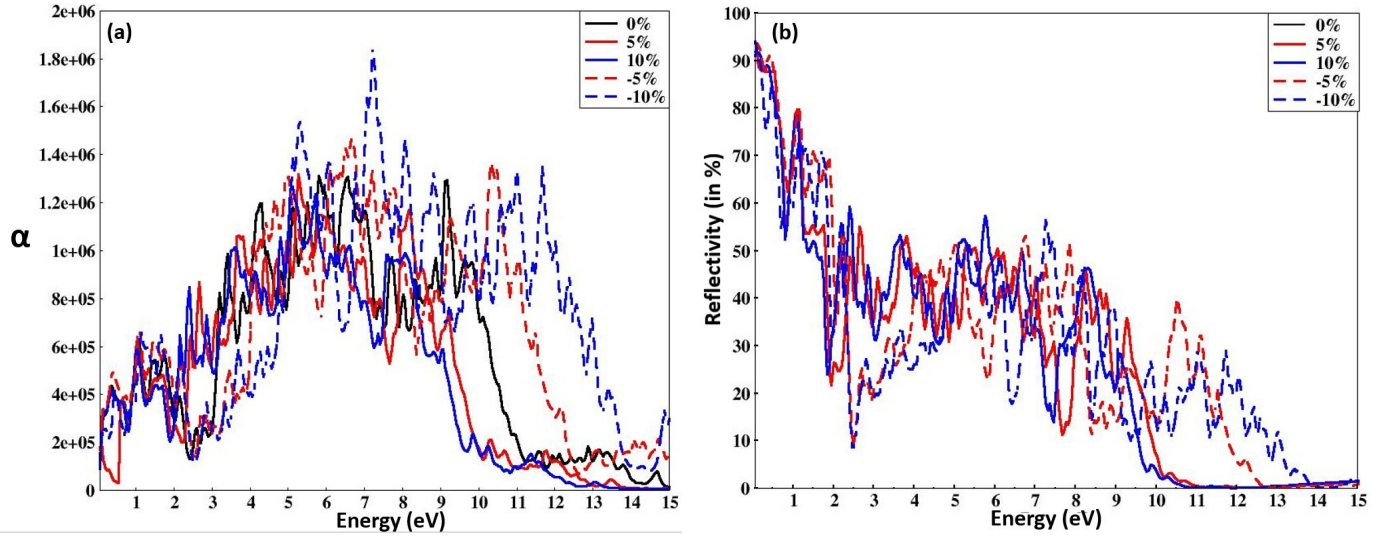
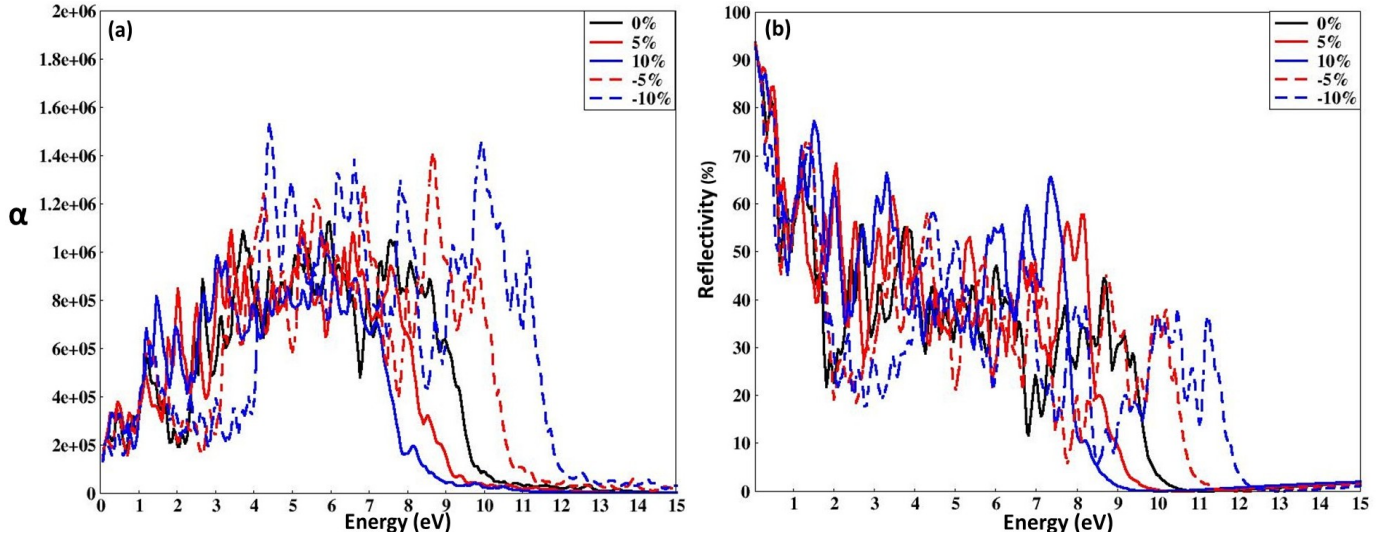Figure 4.9: a) Absorption Coefficient (in cm^{-1}) and b) Reflectivity (in %), for total spin of LiCaB compound.

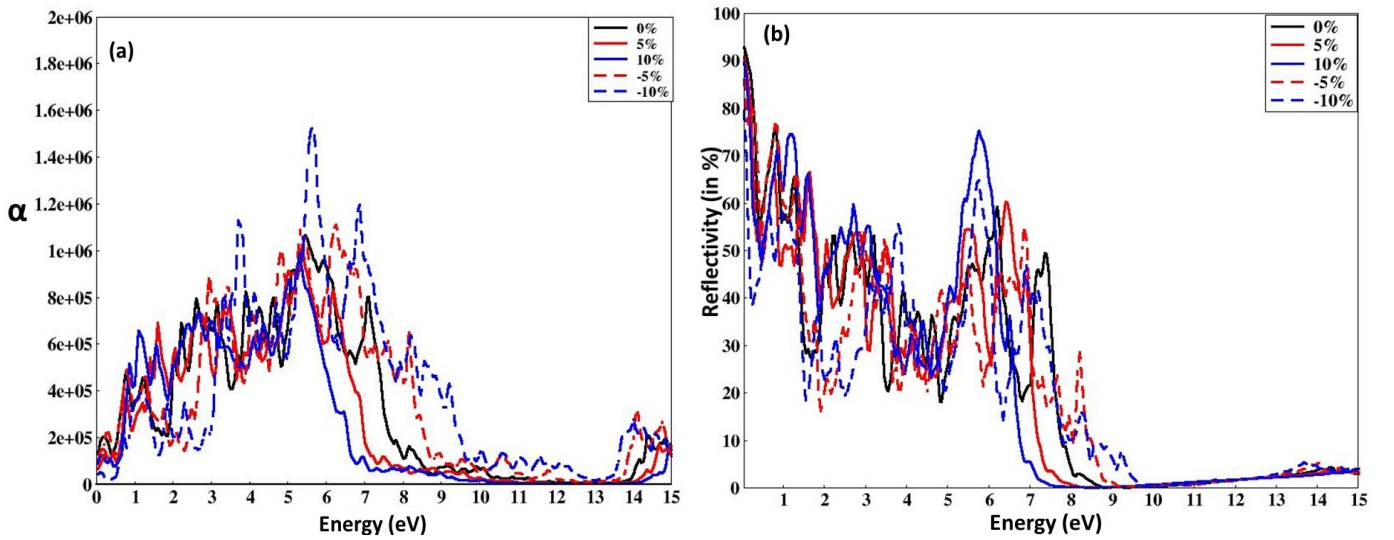Figure 4.10: a) Absorption Coefficient (in cm^{-1}) and b) Reflectivity (in %), for total spin of NaCaB compound.

Figure 4.11: a) Absorption Coefficient (in cm^{-1}) and b) Reflectivity (in %), for total spin of KCaB compound.

The absorption coefficient exhibits threshold values in case of the spin up (semi-conducting) states for both unstrained and strained compounds. The abosorption is found to cover a wide spectral range from near visible to UV Visible regions of the electomagnetic spectra. Moreover, slight red shift of the entire spectrum is observed in going from LiCaB to KCaB alloys. On the other hand, reflectivity values of all the compounds in unstrained condition are around 25%. However, the reflectivity increases with strain for KCaB and also the corresponding reflected spectral range shifts towards low er energy. Figures 4.9-4.11) signify that the metallic nature of the considered half-metallic compounds solely governs their absorption coefficients and reflectivities in total spin states. The absorption coefficients in total spin state cover the entire range from IR to UV Visible regions and the absorption in the UV Visible range is stronger than the others. One noticeable feature of these graphs is that they undergo slight blue shit in energy under applicaiton of isotropic compressive strain while red shift is observed for isotropic tensile strain. Next, reflectivities of all the hH alloys in total spin states are above 90% with similar behaviour as that of absorption coefficient under application of strain. These significantly higher values of reflectivities also suggest that the XCaB (X=Li, Na, K) compounds behave as metallic materials in terms of their optical properties. Moreover, they retain their behaviour even after application of isotropic strain in the range of $\pm 10\%$.

Chapter 5

Summary and Future Scopes

In this work we have theoretically investigated the effect of isotropic tensile strain (upto 10 %) and compressive strain (upto -10 %) on the electronic structure to study the optical properties of hH alloys XCaB (X= Li, Na and K). We have employed density functional theory based calculations for computing both unstrained and strained structures of the material.

It is observed that these half metallic materials with majority spin channel as semiconducting and minority spin channel as metallic. On application of strain, the half matellic nature persists for all the compounds. We notice that the optical characteristics of the class of materials considered for our work, have maximum absorption in the UV region and maximum reflection in the IR region. These high absorption and reflection are the properties of the metallic state of the materials. Analyses of the dielectric function, absorption coefficient and reflectivity parameters show that for the all materials the metallic nature governs their optical properties and they also remain same even under application of isotropic strain of $\pm 10\%$. The nature of the imaginary dielectric function and the high reflectivity values are also due to the fact that intraband transition governs the metallic channel in the lower energy, i.e in IR region.

Based on our observation, we get the hint that the group of 6 VEC half-metallic XCaB (X=Li, Na, K) alloys behave as metallic materials in respect to their optical properties. Under application of strain, although the semiconducting spin up state is slightly tuned, the metallic state remains unaffected and hence the optical behaviour of the materials are similar to that of their unstrained states. This property can find interesting applicaitons in the field of optoelectronics. Moreover, if we want to get the strain effected optical properties of such materials, we have further tune their electronic structures. To achieve this, various methods such as doping, introduction of defects (vacancies etc.), dimensional engineering can be effective. If through significant alteration of electronic structures, pure semiconducting or metallic nature is obtained for such materials, they may find another set of potential applications in different fields such as thermoelectric, magnetic, optical, spintronics etc. The materials show excellent absorption and reflection properties in the IR, visible and UV region, thus making them promising candidates for optoelectronic applications. In sectors where slight strain on the material does not affect the quality, these materials have the potential of gaining its interest. One can modify these materials to intensify its properties by doping, creating vacancies or defects, etc.

Bibliography

[1] T. Graf, C. Felser, S.S.P. Parkin *Simple rules for the understanding of Heusler compounds*, Progress in Solid State Chemistry,39(2011)1-50

[2] R. Farshchi, M. Ramsteiner *Spin injection from Heusler alloys into semiconductors: A materials perspective*, J. Appl. Phys. 113, 191101 (2013)

[3] R.Umamaheshwari, M.Yogeswari, G.Kalpana, *Ab-initio investigation of half-metallic ferromagnetism in half-Heuser compounds XYZ (X= Li, Na, K and Rb: Y= Mg, Ca, Sr and Ba: Z= B, Al and Ga)*, Journal of Magnetism and Magnetic materials 350 (2014) 167-173

[4] J. Pierre, R.V. Skolozdra b, J. Tobola , S. Kaprzyk, C. Hordequin, M.A. Kouacou a, I. Karla, R. Currat a, E. Leli .vre-Berna *Properties on request in semi-Heusler phases*, Journal of Alloys and Compounds 262-263 (1997) 101-107

[5] R. A. de Groot, F. M. Mueller *New Class of Materials: Half-Metallic Ferromagnets*,Phys. Rev. letters 50:25 (1983)

[6] A. Azouaouni, A. Hourmatallah, N. Benzakour, K. Bouslykhane, *First principles study of optoelectronic and thermoelectric properties of LiCaX(X=N, P and As) half-Heusler semiconductors*, Journal of Solid State Chemistry 310 (2022) 123020

[7] Shanming Li, Huaizhou Zhao, Dandan Li, Shifeng Jin, Lin Gu, *Synthesis and thermoelectric properties of half-Heusler alloy YNiBi*, Journal of Applied Physics 117, 205101 (2015)

[8] Dhurba R. Jaishi, Nileema Sharma, Bishnu Karki, Bishnu P. Belbase, Rajendra P. Adhikari, Madhav P. Ghimire, *Electronic Structure and Thermoelectric Properties of Half-Heusler Alloys NiTZ*, arXiv;2009

[9] Binghai Yan, Anne de Visser, *Half-Heusler topological insulators*, *MRS Bulletin* 39, 859–866 (2014).

[10] W. Al-Sawai, H. Lin, R. S. Markiewicz, L. A. Wray, Y. Xia, S. Y. Xu, M. Z. Hasan, A. Bansil, *Topological electronic structure in half-Heusler topological insulators*, Phys. Rev. B 82, 125208 (2010).

[11] Nisha, Hardev S. Saini, Sunita Srivastava, Manish K. Kashyap *Enhanced figure of merit of TaIrGe Half-Heusler alloy for thermoelectric applications under the effect of isotropic strain*, Journal of Solid State Chemistry 303 (2021) 122524

[12] Y. Dhakshayani, G. Suganya, G. Kalpana, *DFT studies on electronic, magnetic and thermoelectric properties of half-Heusler alloys XCaB(X=Li, Na, K and Rb)*, Journal of Crystal Growth 583 (2022) 126550

[13] D. Kieven, R. Klenk, S. Naghavi, C. Felser, T. Gruhn *I-II-V half-Heusler compounds for optoelectronics: Ab initio calculations*, Physical Review B 81, 075208 (2010)

[14] H. Joshi, D.P.Rai, L. Hnamtea, A. Laref, R.K.Thapaa, 'A theoretical analysis of elastic and optical properties of half Heusler MCoSb (M=Ti, Zr and Hf)', Heliyon, 5, e01155 (2019).

[15] S.S.Saeidi, Y.L.Motlagh, J.Jalilian, G.Rezael, B.Vaseghi, *Cooment on "Structural, electronic, magnetic and optical properties of half-Heusler alloys RuMnZ*

(Z= P and As): a first principle study", Journal of Superconductivity and Novel Magnetism (2020) 33:841-845

[16] Nasir Mehmood, Rashid Ahmad, *Structural, Electronic, Magnetic, and Optical Properties of Half-Heusler Alloys RuMnZ (Z = P, As): a First-Principle Study*, J Supercond Nov Magn (2018) 31:233–239

[17] Anuradha Sainia, Shagun Naga, Ranber Singhb, A.A. Alshaikhic, Ranjan Kumar *Unraveling the effect of isotropic strain on the transport properties of half-Heusler alloy LiScGe*, Journal of Alloys and Compounds 859 (2021) 158232

[18] E.H Atmani,I Bziz, N Fazouan and M Aazi *Comparative study by DFT method of structural, electronic and optical properties of monolayer, bilayer and bulk CdS* A 127:878(2021)

[19] M.Jamal, S.S.Nishat, A.Sharif *Effects of transition metal (Fe, Co and Ni) doping on structural, electronic and optical*, Chemical Physics 545 (2021) 111160

[20] Anjami, A., Boochani, A., Elahi, S.M., Akbari, H., *Ab-initio study of mechanical, Half-metallic and optical properties of Mn2 ZrX (X= Ge, Si) compounds*, Results in Physics (2017)

[21] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, J., *QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials*, Journal of Physics: Condensed Matter, 21 (2009) 395502-1 - 395502-19.

[22] D. R. Hamann, *Optimized norm-conserving Vanderbilt pseudopotentials* Phys. Rev. B., 88 (2013) 085117-1 − 085117-10.

[23] J. P. Perdew, K. Burke, M. Ernzerhof, *Generalized Gradient Approximation Made Simple*, Phys. Rev. Lett., 77 (1996) 3865–3868.

[24] H. J. Monkhorst, James D. Pack, *Special points for Brillouin-zone integrations*, Phys. Rev. B., 13 (1976) 5188–5192.

[25] Hirashree Pathak, *DFT study on electronic properties of Half-Heusler compounds XCaB(X=Li,Na,Ca)*, (2022), Department of Physics, Dibrugarh University