First-principles calculations of electronic, optical and elastic Properties of Y_8CoIn_3

Md.Golam Kibria
Materials and Metallurgical Engineering
BUET
Dhaka, Bangladesh
dreamershohag004@gmail.com

Md.Rubaiet Shattique
Materials and Metallurgical Engineering
BUET
Dhaka, Bangladesh
shattique.buet@gmail.com

***Abstract*— A theoretical study of optimized crystal structure with electronic, optical and elastic properties of newly synthesized Y_8CoIn_3 is performed by using the first-principles pseudo-potential plane-wave method within the Generalized Gradient Approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE). It is found that mainly 3d electrons of Yttrium (Y) and Cobalt (Co) contribute to DOS, which can influence the conduction phenomenon. The indirect band gap of this compound is found to be 0.034 eV. The optical properties such as dielectric function, refractive index, absorption coefficient and conductivity are calculated and explained. Based on the calculation of stress tensor it is found that Y_8CoIn_3 possesses anisotropic elastic property. Mechanical properties such as bulk and shear modulus, young's modulus, poison's ratio for Y_8CoIn_3, in the frame work of Voigt-Reuss-Hill, are also calculated. Furthermore, Debye temperature and transverse and longitudinal sound velocities were calculated by using obtained elastic constants.**

Keywords*—Y_8CoIn_3; *first principle method; electronic structure; optical property; stress tensor; Debye temperature.

I. INTRODUCTION

A large number of ternary compounds exist in the rare earth metal rich region of RE-T-In systems. A new rare earth compound is found in the course of investigation of the isothermal ternary section at 870K [1].Y_8CoIn_3 has hexagonal crystal structure, space group P63mc, Pearson code hP24 with 24 formula units. Lattice parameters are given in table I. In this compound cobalt and indium atoms are not attached with each other and with the same type. They are characterized by small coordination number for all atoms .Their structure is similar to PR_8CoGa_3 which belongs to the hexagonal branch of the AIB_2 related structures [1]. Different physical and chemical properties of this compound are now under intense observation due to the presence of d-block element. Still now no experimental data is available for their macroscopic properties. For this reason theoretical investigation of these properties will be helpful for understanding these materials. In this case Ab initio electronic structure method, in the frame of Kohn Sham scheme of the density functional theory helps to explain macroscopic properties. We have calculated electronic properties i.e. band gap, DOS (density of states) as well as optical properties i.e. dielectric function, absorption, refractivity, conductivity for the first time. To investigate mechanical property of this compound we also calculated elastic constants, bulk and shear modulus, young's modulus, poison's ratio, Debye temperature and sound velocities as well.

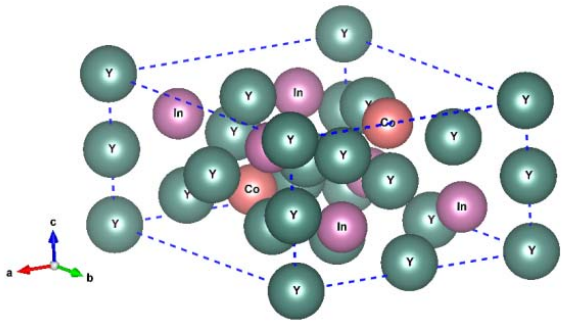

Fig.1. Unit cell of Y_8CoIn_3

II. COMPUTATIONAL DETAILS

The first principle calculations were performed by pseudo-potential plane wave method based on the density functional theory and implemented in (Cambridge Serial Total Energy Package) CASTEP code[2]. In this code Kohn Sham equations are solved within the frame of density functional theory by expanding valance states in terms of basis set of plane waves. The electronic exchange correlation energy is treated under generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE) [3].The interaction between ions and electrons are represented by ultrasoft Vanderbilt-type pseudo-potential [4].The Monkhorst-pack[5] scheme k points grid sampling was set at 4×4×6 to replace integration over the Brillouin zone. The plane wave basis set cut off energy was taken at 420 eV for better convergence. Geometry optimization is achieved by convergence tolerance of total energy 5.0e-6, maximum ionic Hellmann-Feynman force 0.01ev/A, maximum displacements 5.0e-4A^0 and maximum stress component 0.02 GPa.

III. RESULTS AND DISCUSSION

A. Electronic properties

The calculated band structure and density of states of Y_8CoIn_3 at 0 hydrostatic pressure are shown in Fig. 2. The path of Brillouin zone, wave vector k dependent, is taken as Γ(0,0,0), A(0,0,.50), H(-.33,.67,.50), K(-.33,.67,0), Γ(0,0,0), M(0,.50,0), L(0,.50,.50), H(-.33,.67,.50).The indirect band gap is found 0.034 eV. GGA functional underestimates band gap due to many body problems [6]. So, actual band gap may be a little higher. The peak of valance band is at the K point, almost touching Fermi energy. Lowest portion of conduction band lies between G and A point .The metallic behavior of this rare earth compound can be explained from its band structure and density of states (DOS).Localized bands, around -14 eV bellow the Fermi level, are completely filled with Indium (In) 4d states. They do not contribute in bonding and electrical conduction. There is an empty region between 13.1 eV to 8.2 eV. Delocalized valance bands in the region of -4.5eV to -6.5 eV contain 6 bands compose of Y-4d, Y-4p, Y-5s and In-5s states. Delocalized valance bands near Fermi energy extend from 0 eV to -4 eV, mainly occupied by Co-3d, Y-4d states and a little admix of In-5p with Y-4p, Y-5s states. The covalent bond character of Y-In arises from strong hybridization between Y-4d and In-5p states. Same condition exists between Co-3d and In-5p states. Y-Y shows complexity in bonding because of the resonance of 4d electrons near Fermi energy. Anti-bonding states exist as lowest occupied orbitals, above Fermi energy, at 0 eV to 1.7 eV. These are mainly anti-bonding states of Co-3d and Y-4d.

B. Optical properties

The linear optical properties of Y_8CoIn_3 are calculated by using GGA functional. Unfortunately there is no experimental data regarding optical properties found elsewhere. So we calculated optical properties without scissors approximation. Optical properties of materials can directly be calculated from scalar dielectric function. The imaginary part of dielectric function can be calculated by direct numerical evaluations of the matrix elements of the dielectric operator between the occupied states of the VB and unoccupied states of CB [7]

$$\varepsilon_2(\omega) = 2\pi e^2/\Omega\varepsilon_0 \Sigma_{k,\,v,\,c} |\Psi^c_k| \,u.r\, |\Psi^v_k|^2 \delta(E^c_k - E^v_k - E) \quad (1)$$

U is the polarization vector of the incident electric field, ω is the frequency of electromagnetic wave (photon), e and r are the electron's charge and radius vector respectively, ψ^c_k and ψ^v_k are the wave function of conduction band and valance band respectively at k. Real part of the dielectric function can be derived from Kramers-Kronig[5] relation. All optical

$$\varepsilon_1(\omega) = 1 - 2/\pi \int_\infty^0 \varepsilon_2(\omega')\omega' \, d\omega' / \omega'^2 - \omega^2 \quad (2)$$

properties are the output of inter bands and intra bands transition of energy states. Transition is easier in direct band gap material than indirect material. Transition in Y_8CoIn_3 is phonon assisted due to indirect band gap. Calculated results of optical properties (dielectric functions, absorption, refraction, conductivity) at [100] are given in fig. 3.Imaginary part shows single peak for .8 eV which corresponds with maximum peak at .8 eV in conduction band. Single peak in imaginary part directs us that in this compound spin orbit coupling is small. Imaginary dielectric function is related to absorption coefficient i.e. nonzero part of imaginary dielectric function predicts non zero absorption coefficients. For this compound real dielectric is 0 in the range of 10 eV to 11.8 eV and static dielectric function is 10.11.Two shoulders are in absorption, one from 0 eV to 10 eV and another 11.8 eV to 17.3 eV, due to indirect band gap. Maximum peak at 2.3 eV in absorption spectrum corresponds with the distance between maximum peak at valance band to maximum peak at conduction band. Mainly Y-4d, Y-4s, Y-5p and Co-3d electrons excited to conduction band for lower part (0 to 10 eV) of the absorption coefficient and Indium filled 4d electrons are responsible for second part(11.8 eV to 17.3 eV) of the absorption coefficient. Refractive index is related to dielectric function i.e. dielectric function is equal to $\tilde{n}^2$.At zero frequency real part of refractive index is square root of real dielectric. Optical conductivity function can be calculated from the imaginary part of the

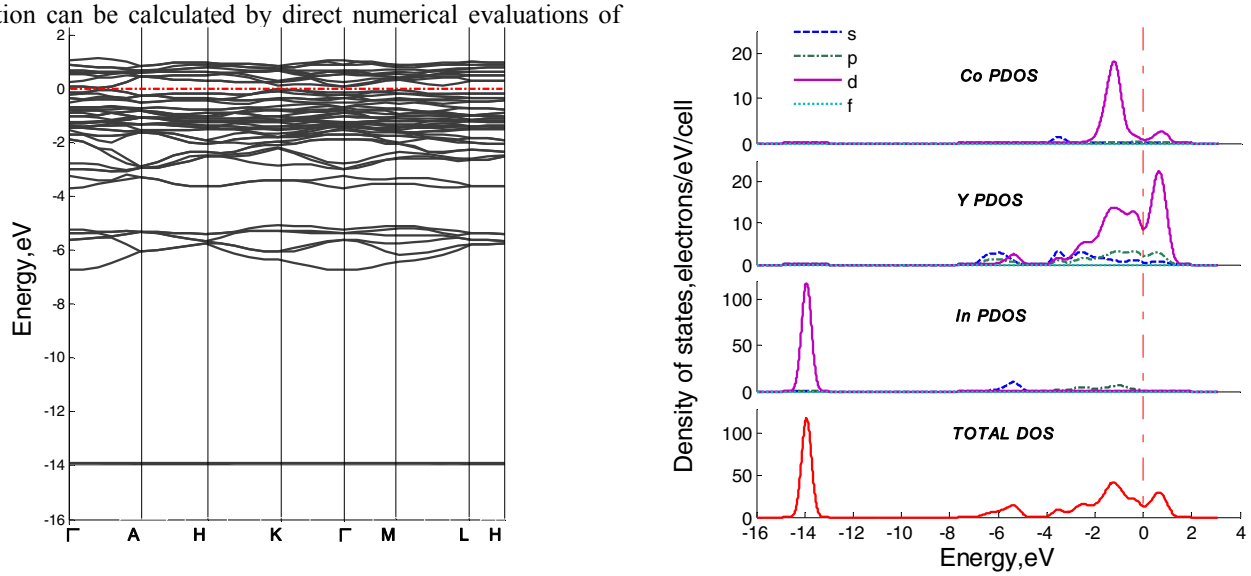

Fig. 2.Band structure and Density of states (DOS) of Y_8CoIn_3

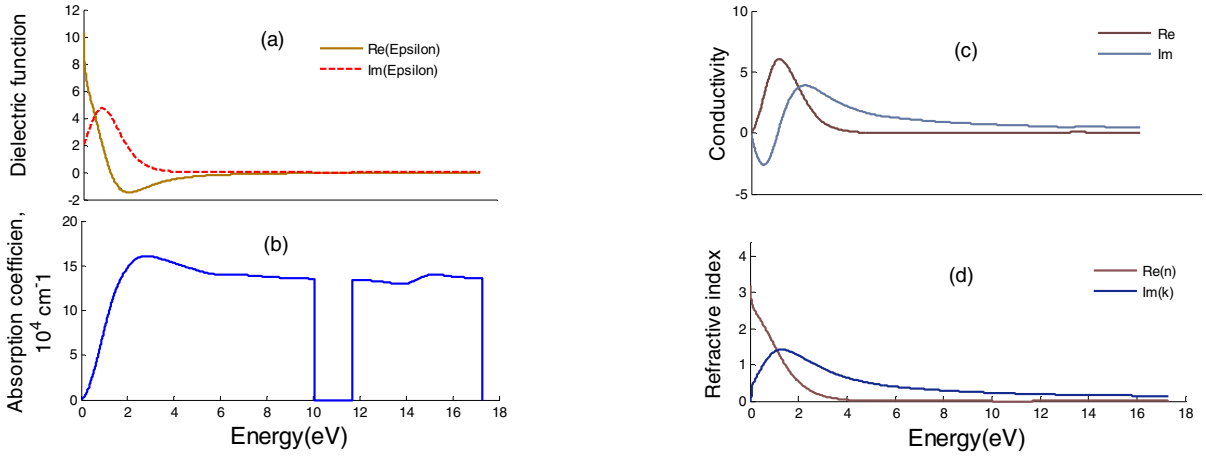

Fig. 3.Dielectric function, absorption, refraction and conductivity of Y_8CoIn_3

dielectric by following equation[8]

$$\sigma(\omega) = \{-(i\omega)\,\varepsilon\,(\omega)\}/4\pi \qquad (3)$$

Single peak in conductivity spectrum corresponds with imaginary dielectric function. The width of conduction curve also corresponds with the width of conduction band.

C. *Elastic properties*

The elastic stiffness C_{ij} relates the stress with a given strain and it describes the derivative of the total energy as a function of lattice strain. Elastic properties of Y_8CoIn_3 at 0 hydrostatic pressure is calculated for the first time. There are various methods for the calculation of elastic constants. For our calculation we used finite strain method. In this method optimized structure is deformed homogenously according to strain patterns with alternating amplitude. After optimizing free parameters stress tensors are calculated. Both stress and strain have three tensile and three shear components. The stiffness C_{ij} forms 6×6 symmetric matrix with a maximum 21 different components such that $\sigma_i=C_{ij}\varepsilon_j$ for small stresses and strains. A hexagonal crystal has six different symmetry elements only five of them are independent such as $C_{66}= C_{11}-C_{12}/2$.Two strain patterns, one with nonzero first and fourth components and another with a nonzero third component, give stresses related to all five independent elastic stiffness for the hexagonal system[9]. We used six amplitude(three positive and three negative) for each strain component with maximum strain value .3%.The calculated elastic properties are presented in table 1. Voigt-Reuss–Hill (VRH) approximation is used for this calculation. So the polycrystalline moduli are defined as the arithmetic mean of the Voigt [10] (B_V, G_V) and Reuss [11] (B_R,G_R) moduli respectively i.e. $B=(B_V+B_R)/2$ and $G=(G_V+G_R)/2$. In Voigt expression B and G are obtained as:

$$B_V= (1/9)\ \{2(C_{11}+C_{12}) + 4C_{13}+C_{33}\} \qquad (4)$$

$$G_V= (1/30)\ \{C_{11}+C_{12}+2C_{33}-4C_{13}+12C_{44}+12C_{66}\} \qquad (5)$$

In Reuss approximation these values are

$$B_R= \{(C_{11}+C_{12})C_{33} -C_{12}^2\}/\ (C_{11}+C_{12}+2C_{33}-4C_{13}) \qquad (6)$$

$$G_R=[(1/5)\{(1/G_{eff})+(2/C_{44})+(2/C_{66})\}]^{-1} \qquad (7)$$

$$G_{eff}=(C_{11}+C_{33}-2C_{13}-C_{66})/3 \qquad (8)$$

Young's modulus E and poison's ratio v of polycrystalline material can be obtained from bulk and shear modulus by following expressions and obtained results are given in table II.

$$E=9BG/\ (3B+G) \qquad (9)$$

$$V=3B-E/6B \qquad (10)$$

Conditions for the mechanical stability for the structure is that $C_{44}>0$, $C_{11}>|C_{12}|$, $(C_{11}+2C_{12})C_{33}>C_{13}^2$[12].This compound is mechanically stable because it satisfies these conditions. Anisotropy of a crystal can be correlated with micro cracks. In terms of elastic constants, elastic anisotropy of this material can be predicted i.e. $A=2C_{44}/C_{11}-C_{12}$ [13].For A =1, materials show complete isotropy but this value can be smaller or greater than 1. For Y_8CoIn_3, this value is 1.19 which directs that this compound shows considerable anisotropy. Compressibility is an important mechanical property which measures the elastic deformation of a material. Linear compressibility coefficient K_a, K_b for this system is equal but not K_c. The ratio between these coefficients i.e. $K_c/K_a=(C_{11}+C_{12}-2C_{13})/C_{33}-C_{13}$ directs us that compressibility along c axis is 1.8 times greater than a axis or b axis. Ductility or brittleness for this system can also

TABLE I. THE CALCULATED ELASTIC STIFFNESS OF Y_8CoIn_3.

a(A^0)	b(A^0)	c(A^0)	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
10.37	10.37	7.01	109.06	41.97	40.50	79.39	39.82	33.55

be determined in terms of Pugh's ratio. If G/B<.5, materials show ductility otherwise brittleness. Pugh's ratio (G/B) .56, gives brittleness for this system. Machinability index i.e. μ_M=B/C_{44} is another way for predicting material's brittleness. This index (1.48) also demonstrates the brittleness of Y_8CoIn_3. The results of calculation from elastic constants can be used for the estimation of Debye temperature.. This parameter is important for the analysis of specific compound, thermal conductivity and melting temperature. This is estimated from Debye-Gruneisen model [14,15] which is expressed as

$$\theta_D = \frac{h}{k} [3n/ 4\pi) (N_A\rho/M)]^{1/3} \upsilon_m \quad (11)$$

h and k are plank's and Boltzmann's constants respectively, n is the formula unit per cell, N Avogadro's number, ρ density , m molecular mass and υ_m average sound velocity in the compound. Average sound velocity is expressed follows

$$\upsilon_m=[1/3(2/\upsilon_t^3+1/\upsilon_l^3)]^{-1/3} \quad (12)$$

where υ_t and υ_l are transverse and longitudinal sound velocity through compound. υ_t and υ_l can be determined from bulk and shear modulus as $\upsilon_t=\sqrt{(3B+4G/3\rho)}$ and $\upsilon_l=\sqrt{(G/\rho)}$. Calculated results of sound velocities and Debye temperature are given in following table II.

TABLE II . DENSITY ρ(g/cm^2), LONGITUDINAL VELOCITIY υ_l (m/s) ,TRANSVERSE VELOCITIY υ_t (m/s) and AVERAGE VELOCITIY υ_m(m/s) WITH DEBYE TEMPERATURE Θ_D(K) OF Y_8CoIn_3.

ρ	υ_l	υ_t	υ_m	θ_D
5.68	4289	2433	2705	337.64

IV. CONCLUSION

In this work we have calculated electronic, optical and elastic properties of Y_8CoIn_3 by using pseudo-potential plane wave method. We have predicted that this material shows indirect small band gap and exhibits metallic behavior. PDOS reveals that mainly Y-4d and Co-3d form valance states and Y-4d dominates conduction states. Optical properties i.e. dielectric function, absorption, refractivity, conductivity are calculated and explained. Analyzing optical function through [100] direction it is found that, this compound has low dielectric constant. Elastic constants are calculated and from these results bulk and shear modulus of Y_8CoIn_3 are also obtained. From the results of elasticity we predicted that this compound is anisotropic and brittle. This compound also shows mechanical stability. Finally Debye temperature and sound velocities through this compound are also calculated from obtained elastic constants.

REFERENCES

[1] M. Dzevenko, I. Bigun, M. Pustovoychenko , L. Havela and Ya. Kalychak,"Rare-earth rich indides RE_8CoIn_3 (RE = Y, Dy-Tm, Lu)," Intermetallic: Elsevier , vol. 38, pp. 14-18, 2013.

[2] S. J. Clark, M. D. Segall, M. J. Probert, C. J. Pickard, P. J. Hasnip and M. C. Payne,"First principles methods using CASTEP," Z. Kristallogr, vol. 220, pp. 567-570, 2005.

[3] J. P. Perdew, K. Burke and M. Ernzerhof,"Generalized Gradient Approximation Made Simple," Phys. Rev. Lett., vol. 77, pp. 3865-3868, 1996.

[4] D. Vanderbilt, "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism," Phys. Rev. B, vol. 41, pp. 7892, 1990.

[5] H. J. Monkhorst and J. D. Pack,"Special points for Brillouin-zone integrations,"Phys. Rev. B ,vol. 13, pp. 5188, 1976.

[6] M.G. Brik,"First-principles calculations of the structural, electronic, optical and elastic properties of the CuYS2 semiconductor," J. Phys.: Condens.Matter, vol. 25, pp. 345802, 2013.

[7] S. Saha, T.P. Sinha and A. Mookerjee,"Electronic structure,chemical bonding and optical properties of paraelectric BaTiO3," Phys Rev B,vol. 62, pp. 8828, 2000.

[8] A.Boukortt, S.Berrah, R.Haynd, A.Zaoui , "First-principle calculation of the optical properties of zinc-blende Zn1-xCdxSySe1-y," PhysicaB, vol. 405, pp. 763–769, 2010.

[9] V Milman, M C Warren, ,"Elasticity of hexagonal BeO," J. Phys.: Condens. Matter, vol. 13, pp. 241–251, 2001.

[10] V.V. Brazhkin.,"High-pressure synthesized materials: treasures and hints,"High Pressure Res., vol. 27, pp. 333-351, 2007.

[11] J.J. Gilman, Electronic Basis of the Strength of Materials, Cambridge University Press:Cambridge, U.K., 2003.

[12] M. Born,K. Huang, Dynamical Theory of Crystal Lattices, Clarendon, Oxford, 1956.

[13] C. M. Zener, Elasticity, Anelasticity of metals, University of Chicago Press, Chicago, 1948.

[14] O.L. Anderson,"A simplified method for calculating the debye temperature from elastic constants,"J. Phys. Chem. Solids,vol. 24 , pp. 909−917,1963

[15] A. A. Marmalyuk, R. Kh. Akchurin and V. A. Gorbylev,"Theoretical Calculation of the Debye Temperature and Temperature Dependence of Heat Capacity of Aluminum, Gallium and Indium Nitrides," High Temperature,Vol.36,pp.817–819,1998.