Advances in Physics Theories and Applications
ISSN 2224-719X (Paper) ISSN 2225-0638 (Online)
Vol.19, 2013 - Selected from International Conference on Recent Trends in Applied Sciences with Engineering Applications
www.iiste.org

First Principles Study of Structural, Electronic, Elastic and Mechanical Properties of $GdSn_3$ and $YbSn_3$ Intermetallic Compounds

Jisha Annie Abraham[1], Gitanjali Pagare[1,*] Sunil Singh Chouhan[1] and S.P. Sanyal[2]
[1]Department of Physics, Government M. L. B. Girls P. G. Autonomous College, Bhopal 462002, India
[2]Department of Physics, Barkatullah University, Bhopal 462026, India
*Corresponding Author E-mail: gita_pagare@yahoo.co.in

Abstract
First principles study of structural, electronic, elastic and mechanical properties of ferromagnetic $GdSn_3$ and non-magnetic $YbSn_3$ rare-earth intermetallics, which crystallize in $AuCu_3$-type structure, is performed using density functional theory based on full potential linearized augmented plane wave (FP-LAPW) method. The ground state calculations are carried out within PBE-GGA, PBE-sol GGA and LSDA approximations for the exchange correlation potential. The calculated ground state properties such as lattice constants and bulk moduli agree well with the experiment as well as other theoretical results. We report elastic constants for these compounds for the first time. Both these compounds are found to be ductile in nature. The computed electronic band structures show metallic character. We also report mechanical properties of these compounds for the first time.
Keywords: Rare-earth; Density functional theory; Elastic constants.

1. Introduction

Rare earth intermetallic systems present a great diversity of magnetic behaviors, often associated with complex magnetic phase diagrams as a function of temperature and applied magnetic field. The rare-earth metals have high magnetic moments and a diverse range of magnetic structures . Their magnetic properties are determined by the occupancy of the strongly localized '4*f*' electronic shells, while the outer '*s–d*' electrons determine the bonding and other electronic properties. Rare earth based intermetallics are of considerable technological and scientific interest due to extra ordinary magnetic properties and industrial applications. These properties are governed by different types of interactions involving the highly correlated and strongly localized '4*f*' states of rare earth and the '*d*' states of transition metal atoms, which are comparatively weakly correlated and more delocalized and also the valence states of R atoms, which are expected to be the mediators of indirect exchange coupling [1, 2].

$GdSn_3$ and $YbSn_3$ belong to the family of Rare earth tristannide $RESn_3$ compounds. These systems have attracted a great deal of interest because of their salient features such as valence fluctuations, magnetic moment formation, crystal field effects or multiaxial magnetic structures [3]. An experiment has been conducted by Miller and Hall [4] to synthesize heavy rare-earth element tristannide $LnSn_3$ (*Ln*=Tb, Dy, Ho, Er, and Y) compounds using a high pressure technique. $TbSn_3$ and YSn_3 have been synthesized at P = 1–7GPa and T = 400°C–1300°C. These two compounds also have a cubic $AuCu_3$ type structure with a lattice constant a = 0.466 nm and 0.467 nm, and a density of 8.45 g/cm^3 and 7.27 g/cm^3, respectively[5]. Superconducting state in YSn_3 with $AuCu_3$-type structure has been studied by Kawashima *et. al.* [6]. Their electric field gradients were also calculated. Crystal fields and magnetic properties of $NdSn_3$, $NdPb_3$ and $NdIn_3$ have been studied by Lethuillier *et. al.*[7]. High magnetic field properties of $GdIn_3$ have been investigated by Kletowski *et. al.* [8]. Interband optical transitions in $CeSn_3$ and $LaSn_3$ have been studied by measuring and calculating the optical conductivities of these compounds by Kim [9]. Temperature dependence of magnetic fluctuations in the intermediate valence system $CeSn_3$ has been reported by Capellmann *et. al.*[10]. Valency of rare earths in RIn_3 and RSn_3 and *ab-initio* analysis of electric field gradients have been investigated by Asadabadi *et. al.*[11]. The structural properties such as lattice parameter and bulk modulus of $SmSn_3$, $EuSn_3$, $GdSn_3$, $TmIn_3$, $YbIn_3$ and $LuIn_3$ using LDA, GGA and GGA + spin polarized approximations have been calculated using Wien97 code [12]. Observation of the de haas-van alphen effect in powdered $YbSn_3$ and $CaSn_3$ has been reported by Klaasse *et. al* [13]. $YbSn_3$ shows a superconducting transition at around 3.6 K [14].

The rare earth intermetallics $GdSn_3$ and $YbSn_3$ compounds crystallize in cubic $AuCu_3$-type structure (space group symmetry of *Pm3m* (No.221)). In the present work, we report the structural, electronic, elastic and mechanical properties of $GdSn_3$ and $YbSn_3$ compounds using density functional theory. The elastic constants of these compounds are reported for the first time. A brief description of the computational details is outlined in Section 2 while Section 3 covers the results, followed by discussion.

2. Computational Method.

The present calculations have been performed using full potential linear augmented plane wave (FP-LAPW)

method as implemented in WIEN2k package [15]. In this method, the basis set is obtained by dividing the unit cell into non-overlapping spheres and an interstitial region. Here PBE-GGA, PBE-sol GGA and LSDA is used for the exchange and correlation effects [16, 17, 18]. The values of $K_{max} \times R_{MT} = 7.0$ and $l_{max} = 10$ are kept throughout the calculation. A dense mesh of 10×10×10 k points is used and tetrahedral method [19] has been used for the Brillouin Zone integration. The calculations are iterated until the total energies are converged below 10^{-4} Ry. The total energies are calculated as a function of volume and fitted to Birch-Murnaghan equation of state (third order) [20] to obtain the ground state properties like zero-pressure equilibrium volume.

The elastic moduli require knowledge of the derivative of the energy as a function of the lattice strain. The symmetry of the cubic lattice reduces the 21 elastic constants to three independent elastic constants namely C_{11}, C_{12} and C_{44}. The elastic stability criteria for a cubic crystal at ambient conditions are $C_{11}+2C_{12} > 0$, $C_{44} > 0$ and $C_{11}- C_{12} > 0$ and $C_{12} < B < C_{11}$. In the present work, the elastic constants are calculated using the tetrahedral and rhombohedral distortions on the cubic structure using the method developed by Thomas Charpin integrated it in the WIEN2k package [15]. The systems are fully relaxed after each distortion in order to reach the equilibrium state. C_{44} is proportional to the shear modulus and can be used as a measure of shear resistance.

3. Result and discussion

3.1. Ground state properties

The spin polarized electronic band structure calculations have been carried out to obtain the total energy of the $GdSn_3$ and $YbSn_3$ intermetallics using the first principles FP-LAPW method. In order to calculate the ground state properties, the total energies are calculated in $AuCu_3$ type structure for different volumes around the equilibrium cell volume V_0. The calculated total energies are fitted to the Birch-Murnaghan equation of state to determine the ground state properties like lattice constant (a_0), bulk modulus (B) and its pressure derivative (B′) at minimum equilibrium volume V_0.

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

Pressure is obtained by taking volume derivative of the total energy

$$P(V) = \frac{B}{B'}\left[\left(\frac{V}{V_0}\right)^{B'} - 1\right]$$

and $B' = \partial B/\partial P$

The calculated ground state properties are given in Table 1, and compared with the experimental data and available other theoretical calculations [12, 21]. It is seen from Table 1 that our calculated values of lattice parameter using PBE-GGA are in better agreement with the experimental results than those obtained using PBE-sol GGA and LSDA calculations. The better prediction of experimental results by GGA has also been observed in most rare-earth metals and is believed to be due to the fact that the nonlocality of exchange and correlation is better taken into account by GGA than LDA [22]. Spin polarized calculations does not practically affect the ground state properties of $YbSn_3$ due to the presence of almost fully occupied '*f*' shell of Ytterbium. The calculated total magnetic moment (μ_{tot}) of both the compounds are given in Table 2. Furthermore, as, to our knowledge, no experimental data for the bulk modulus and its derivative have been reported yet, our results can serve as a prediction for future studies.

3.2. Electronic properties:

The self consistent spin polarized band structures (BS) along the high symmetry directions for majority and minority spins for $GdSn_3$ and $YbSn_3$ compounds are presented in Figure 1.The total and partial densities of states (DOS) for these compounds at ambient pressure are also calculated and presented in Figure 2. The Fermi level is shown at the origin. It is clear from the figures that the lowest lying bands below -20eV are due to Sn '*d*' like states in $GdSn_3$. The bands which lies in between -11 eV and -5 eV are due to Sn '*s*' like states. There is a flat band below the Fermi level around -4 eV which are mainly due to Gd '*f*' states in majority spin which gets shifts above the Fermi level in minority spin. The bands just below the Fermi level are due to Sn '*p*' and Gd '*d*' states. The strong hybridization of Sn '*p*' and Gd '*d*' states at the Fermi level shows the metallic character of these compounds. Due to this metallic character, we found finite DOS (1.325 states/eV) at the Fermi level for $GdSn_3$ in which major contribution is due to Sn '*p*' states. A peak is observed around 2.5eV above the Fermi level which is due to '*d*' like states of Gd in both the spins. We can see an increase in finite DOS (1.725 states/eV) in minority spin due to delocalization of Gd '*f*' states. On the whole, the band profiles are seen to be almost same for both compounds except for certain changes. The electronic band structure for $YbSn_3$ shows similar behavior in both majority and minority spins. The lowest lying band in between -11 eV and -5eV is due to '*s*' like states of Sn. There is a flat band lying just below the Fermi level which is due to the '*f*' like states of

Yb. There is hybridization of Yb '*f*' states and Sn '*p*' states at the Fermi level shows the metallic character of these compounds. A peak is observed around 5eV above Fermi level which is due to '*d*' like states of Yb in both the spins. We found finite DOS (0.04 states/ eV) at the Fermi level for $YbSn_3$ in which major contribution is due to Sn '*p*' states.

3.3. Elastic properties

The elastic constants determine the response of the crystal to external forces, as characterized by bulk modulus, shear modulus, Young's modulus, and Poisson's ratio, and obviously play an important role in determining the strength and stability of materials. Elastic properties are also linked to sound velocity and Debye temperature.We have calculated the elastic constants of the $GdSn_3$ and $YbSn_3$ compounds in $AuCu_3$ structure using PBE-GGA as exchange correlation at ambient pressure using the method developed by Thomas Charpin and integrated it in the WIEN2k package [15]. The calculated values of elastic constants are given in Table 2. In the absence of any available measured data in the literature, these elastic constants could not be compared. It can be noted that our calculated elastic constants satisfy the stability criterions: $C_{11}- C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$, $C_{12} < B < C_{11}$, which clearly indicate the stability of these compounds in $AuCu_3$ structure.

3.4. Mechanical properties

Elastic constants can be used to determine mechanical properties such as Young's modulus (*E*), shear modulus (G_H), Poisson's ratio (σ), and anisotropic ratio (*A*) for useful applications. These are fundamental parameters which are closely related to many physical properties like internal strain, thermo elastic stress, sound velocity, fracture, toughness. We have calculated these properties of these compounds and presented in Table 2. The shear modulus G_H describes the material's response to shearing strain using the Voigt–Reuss–Hill (VRH) method [23-25]; the effective modulus for the polycrystals could be approximated by the arithmetic mean of the two well known bounds for monocrystals.

The bulk and shear modulus, defined as

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad \text{and} \quad G_H = \frac{\frac{C_{11} - C_{12} + 3C_{44}}{5} + \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})}}{2}$$

Another important parameter is the elastic anisotropic factor A, which gives a measure of the anisotropy of the elastic wave velocity in a crystal and it is given as:

$$A = \frac{2C_{44}}{C_{11} - C_{12}}$$

which is unity for an isotropic material. It also tells more about the structural stability and it is correlated with the possibility of inducing micro cracks in the materials.

The calculated elastic anisotropic factor for both the compounds is greater than 1, which indicates that these compounds are not elastically isotropic. As suggested by Pugh [26], if $B/G_H > 1.75$; a material behaves in a ductile manner. From Table 2, it can be seen that the highest value of B/G_H is 2.64 for $YbSn_3$ indicating it more ductile than $GdSn_3$. Ganeshan *et.al.* [27] have established a correlation between the binding properties and ductility. The bond character of cubic compounds is explained with respect to their Cauchy pressure (C_{12}–C_{44}). The $YbSn_3$ has a highest positive Cauchy pressure; resulting strong metallic bonding (ductility) in it as compared to $GdSn_3$.

Young's modulus is defined as the ratio of stress and strain, and is used to provide a measure of the stiffness of the solid, *i.e.,* the larger value of *E*, the stiffer is the material. It can be seen from Table 2 that the highest value E occurs for $GdSn_3$ implying it to be stiffer as compared to $YbSn_3$.

Young's modulus (E) and Poisson's ratio (σ) is given by

$$E = \frac{9BG_H}{3B + G_H} \quad \text{and} \quad \sigma = \frac{(3B - E)}{6B}$$

The value of Poisson's ratio, found to be ≈ 0.33 in metallic materials [28]. It is observed from Table 2 that the value of Poisson's ratio lies in between 0.325 and 0.332 for $GdSn_3$ and $YbSn_3$. It shows that metallic contributions to the atomic bonding are dominant for these compounds.

The longitudinal and transverse sound velocities (v_l and v_t) are obtained by using these elastic constants as follows:

$$v_l = \sqrt{\frac{\left[C_{11} + \frac{2}{5}(2C_{44} + C_{12} - C_{11})\right]}{\rho}} \quad \text{and} \quad v_t = \sqrt{\frac{\left[C_{44} - \frac{1}{5}(2C_{44} + C_{12} - C_{11})\right]}{\rho}}$$

here C_{11}, C_{12} and C_{44} are second order elastic constants and ρ is mass density per unit volume, and the average sound velocity v_m and Debye temperature is approximately calculated from [29, 30, 31]:

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3}+\frac{1}{v_l^3}\right)\right]^{-1/3} \quad \text{and} \quad \theta_D = \frac{h}{K_B}\left[\frac{3n}{4\pi V_a}\right]^{1/3} v_m$$

where h is Planck's constant, K_B is Boltzmann's constant, V_a is the average atomic volume.
We have calculated the average elastic sound velocities, Debye temperatures as well as the densities for both the compounds by using the calculated elastic constants and are presented in Table 2. The elastic sound velocities and Debye temperature of $GdSn_3$ is found to be higher as compared to $YbSn_3$.

Conclusion

In conclusion, we have systematically studied the structural, electronic, elastic and mechanical properties of $GdSn_3$ and $YbSn_3$ compounds using FP-LAPW method based on density functional theory, within GGA, PBE-sol GGA and LSDA approximations. Our results on the structural, electronic, elastic and mechanical properties for these compounds are in agreement with available theoretical and experimental results. The ground state properties such as bulk moduli and lattice parameters are computed and compared with the preceding theoretical and other experimental results, which shows good agreement. The calculated elastic constants (C_{11}, C_{12} and C_{44}) have shown that $GdSn_3$ and $YbSn_3$ are elastically stable in the $AuCu_3$ structure. Using these elastic constants, Young's modulus (E), the shear modulus (G_H), Poisson's ratio (σ) and anisotropic ratio (A) are also reported. In present study we found $B/G_H > 1.75$ and $C_{12} - C_{44} > 0$; for both the compounds which implies that both the compounds are ductile in nature. The computed electronic band structures show metallic character. We also report mechanical properties of these compounds for the first time, which will be tested in the future experimentally and theoretically.

Acknowledgements

The authors are thankful to UGC (New Delhi) for the financial support for Major Research Project. SPS is thankful to UGC (SAP).The authors are thankful to Dr. M. Rajagopalan, Emeritus Scientist, Crystal Growth Centre, Chennai for valuable discussions.

References

[1] Buschow, K.H.J. (1980). *Ferromagnetic Materials*, 1, 297
[2] Franse, J.J.M, & Radvansky, R.J. (1993). *Ferromagnetic Materials*, 7, 307
[3] Lawrence, J.M., Riseborough, P.S., & Parks, R.D. (1981). *Reports on Progress in Physics*, 44, 1
[4] Miller, K., & Hall, H. T. (1972). *Inorganic. Chemistry,* 11, 1188
[5] Tonkov, E. Y. **(**1992). *High Pressure Phase Transformations: A Handbook.* (2nd ed.)
[6] Kawashima, K., Maruyama, M., Fukuma, M., & Akimitsu. J. (2010). *Physical Review B***,** 82, 094517
[7] Lethuillier, P., & Pierre, J. (1975). *Le Journal De Physique*, 36, 329
[8] Kletowski, Z., Czopnik A., Tal A., & de Boer, F.R. (2000). *Physica B* , 281 & 282,163-164
[9] Kwang Joo Kim. (1992). Journal of *Physics.: Condensed Matter,* 4, 8039-8044
[10] Capellmann, H., Brown, P.J., Johnson, S.M., Ziebeck, K.R.A., & Booth, J.G. (1985). *Journal of Magnetism and Magnetic Materials*, 49, 137-144
[11] Asadabadi, S.J., Cotteneer, S., Akbarzadeh, H., Saki, R., & Rots, M. (2002). *Physical Review B*, 66, 195103
[12] Asadabadi, S.J. , & Akbarzadeh, H. (2004). *Physica B* , 349**,** 76–83
[13] Klaasse, J.C.P.,.Meijer, R.T.W, & de Boer, F.R. (1980). *Solid State Communications*, 33 ,1001-1002
[14] Grechnev, G.E., Panfilov, A.S., Svechkarev, I.V., Buschow, K.H.J, & Czopnik, A. (1995). *Journal of Alloys and Compounds* , 226 , 107-112
[15] Blaha, P., Schwarz, K., Madsen, G.K.H., Kuasnicka, D.J., & Luitz, WIEN2K, *An Augmented Plane Wave+ Local Orbitals Program for Calculating Crystal Properties.* (2001). K. Schwarz Technical Universitat, Wien, Austria, ISBN 3-9501031-1-2
[16] Perdew, J.P., Burke, & Ernzerhof, K., M. (1996). *Phys. Rev. Lett*., 77, 386 -3868
[17] Perdew, J.P., Ruzsinszky, Gábor, A., Csonka, I., Vydrov, Scuseria, A., Constantin, L.A., Zhou, X., & Burke, K. (2008). *Physical Review Letters*, 100, 136406
[18] Hohenberg, P., Kohn, W., (1964). *Physical Review,* 136, *B*864-B871
[19] Monkhorst, H.J. , & Pack, J.D. (1976). *Physical Review B* , 13, 5188
[20] Birch, F.(1938). *Journal of Applied. Physics*, 9, 279
[21] Landelli, A., & Palenzona, A. (1979). *Handbook on the Physics and Chemistry of Rare Earths.* **(**2nd ed.). Amsterdam: North-Holland.
[22] Delin, A., Fast, L., & Johanson, B. (1998). *Physical. Review B* , 8, 58
[23] Hill, R. (1952). *Proceedings of the Physical Society of London A* , 65, 349–354

[24] Voigt, W. (1889). *Annals of Physics*, 38, 573–587
[25] Reuss, A., & Angew, Z. (1929). *Math. Phys*., 9, 49–58
[26] Pugh, S.F. (1954). *Philosophical Magazine*, 45 , 823–843
[27] Ganeshan, S.,Shang, S.L., Zhang, Wang,Y., Mantina, M., &Liu, Z.K.(2009).*Intermetallics*,17, 313–318
[28] Haines, J., Léger, J.M., & Bocquillon, G. (2001). *Annual Review of Material Research*, 31, 1–23
[29] Sun, Z., Li, S., Ahuja, R., & Schneider, J. M. (2004). *Solid State Commun.*,129, 589-592
[30] Jasiukiewicz, C., & Karpus, V. (2003). *Solid State Commun.*, 128, 167-169
[31] Wachter, P., Filzmoser, M., & Rebizant, J. (2001). *Phys. B*, 293, 199-223

Table 1. Calculated lattice parameter a_0 (Å), Bulk modulus B (GPa), its pressure derivative (B′) and elastic constants (C_{11}, C_{12}, C_{44}) of $GdSn_3$ and $YbSn_3$ in $AuCu_3$ structure

Solid	Work	a_0 Å	B (GPa)	B'	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
$GdSn_3$	PBE GGA	4.681	58.03	4.64	65.59	53.56	50.73
	PBE-sol GGA	4.644	67.45	3.95	-	-	-
	LSDA	4.595	71.66	4.29	-	-	-
	Expt.	4.678[a]	-	-	-	-	-
	Oth. GGA	4.683[b]	64.32[b]	4.69[b]	-	-	-
	LDA	4.513[b]	62.55[b]	2.95[b]	-	-	-
$YbSn_3$	PBE GGA	4.702	52.45	4.49	62.58	44.10	30.70
	PBE-sol GGA	4.621	59.38	5.06	-	-	-
	LSDA	4.564	67.08	4.50	-	-	-
	Expt.	4.681[a]	-	-	-	-	-
	Oth.	-	-	-	-	-	-

[a] Ref. [21], [b] Ref. [12]. Pre. - Present, Expt. - Experiment, Oth. – Other Theoretical calculations.

Table 2. Calculated Young's modulus (E), shear modulus (G_H), anisotropic factor (A), Poisson's ratio (σ), B/G_H ratio, Cauchy's pressure (C_{12} - C_{44}) , magnetic moment (μ_{tot}), density (ρ), longitudinal (v_l), transverse (v_t), average elastic wave velocities (v_m) and Debye temperature (θ_D) of $GdSn_3$ and $YbSn_3$ compounds.

Solid	E (GPa)	G_H (GPa)	A	σ	B/G_H	C_{12} - C_{44} (GPa)	μ_{tot} (μ_B)	ρ x 10^3 (kg/m^3)	v_l (m/s)	v_t (m/s)	v_m (m/s)	θ_D (K)
$GdSn_3$	60.43	22.80	8.44	0.32	2.52	02.83	6.81	5.736	4203	2392	2657	147.10
$YbSn_3$	50.66	19.01	3.32	0.33	2.64	13.40	0.00	5.981	3651	1923	2148	119.38

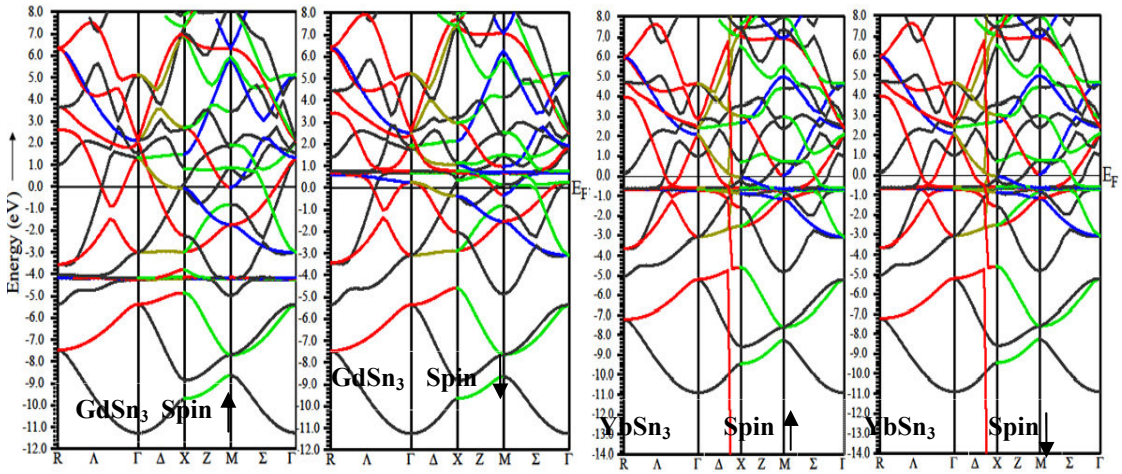

Figure 1. Band structure of $GdSn_3$ and $YbSn_3$ in both majority and minority spin channels.

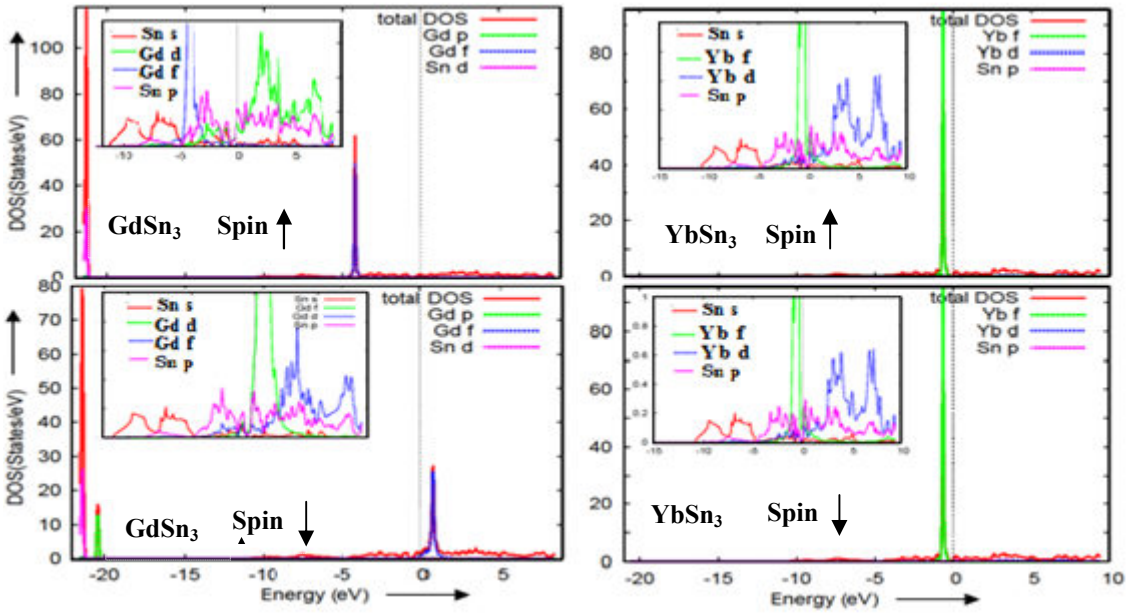

Figure 2. Density of states of $GdSn_3$ and $YbSn_3$ in both majority and minority spin channels.

This academic article was published by The International Institute for Science, Technology and Education (IISTE). The IISTE is a pioneer in the Open Access Publishing service based in the U.S. and Europe. The aim of the institute is Accelerating Global Knowledge Sharing.

More information about the publisher can be found in the IISTE's homepage: http://www.iiste.org

CALL FOR PAPERS

The IISTE is currently hosting more than 30 peer-reviewed academic journals and collaborating with academic institutions around the world. There's no deadline for submission. **Prospective authors of IISTE journals can find the submission instruction on the following page:** http://www.iiste.org/Journals/

The IISTE editorial team promises to the review and publish all the qualified submissions in a **fast** manner. All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Printed version of the journals is also available upon request of readers and authors.

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library , NewJour, Google Scholar