



Mechanical and phonon properties of the superhard LuB_2 , LuB_4 , and LuB_{12} compounds

E. Deligoz^{a,*}, H. Ozisik^a, K. Colakoglu^b, G. Surucu^b, Y.O. Ciftci^b

^a Aksaray University, Department Of Physics, 68100, Aksaray, Turkey

^b Gazi University, Department Of Physics, Teknikokullar, 06500, Ankara, Turkey

ARTICLE INFO

Article history:

Received 4 August 2010

Received in revised form

30 September 2010

Accepted 6 October 2010

Available online 14 October 2010

PACS:

62.20.-x

63.20.D-

Keywords:

Mechanical properties

Lattice dynamical properties

Diborides

ABSTRACT

We have studied structural, elastic, and lattice dynamical properties of the LuB_2 , LuB_4 , and LuB_{12} compounds by using the plane-wave pseudopotential approach to the density-functional theory within the generalized gradient approximation. We have considered three different crystal structures of LuB_x : LuB_2 ($P6/mmm$), LuB_4 ($P4/mbm$), and LuB_{12} ($Fm-3m$). The most stable structure is found to be tetragonal ($P4/mbm$) structure. The comparative results on the basic physical parameters such as lattice constants, bulk modulus, bond distances, elastic constants, shear modulus, Young's modulus, and Poisson's ratio are reported. Also, we have predicted that LuB_4 and LuB_{12} compounds are potential superhard materials. Furthermore, the phonon dispersion curves and corresponding phonon density of states (DOS) are computed for considered phases. Our structural and some other results are in agreement with the available experimental and other theoretical data.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Ultra hard materials are used in many applications, from cutting and polishing tools to wear-resistant coatings [1]. Unfortunately, almost all ultra hard materials (diamond, cubic BN, etc.) are expensive because they either occur naturally in limited supplies or have to be made at high pressure synthetically [2]. Therefore, intense research efforts have been carried out to design ultra hard materials [1,2]. A promising approach to design superhard materials is to combine transition metals possessing a high bulk modulus with small, covalent bond forming atoms such as boron, carbon, nitrogen or oxygen [1,3].

The boron–boron bonds in rare-earth borides containing more than 40% boron are responsible for the high hardness, melting points, and characteristic temperatures of these materials [4]. The presence of rare-earth metals in the boride lattice leads to a wide diversity of electrical and magnetic properties [5]. The rare-earth borides such as diborides (XB_2), tetraborides (XB_4), and dodecaborides (XB_{12}) have attracted a lot of attention over the years as a rich class of materials which exhibit various phenomena of

f-electron magnetism [6–11]. For example, rare-earth borides possess good emissive properties and are used as cathode materials in emission electronics [11].

LuB_2 , LuB_4 , and LuB_{12} belong to the family of rare-earth borides compounds and there exist intense theoretical and experimental studies [11–24] dealing with the structural, elastic, and phonon properties which are our present interest. Recently, LuB_2 compound in $P6/mmm$ structure has been synthesized [11] successfully, and the magnetic properties have been investigated by Mori et al. [12]. Electronic structure and bulk properties of LuB_{12} (UB_{12} -type) have been reported by Grechnev et al. [13]. Nemkovski et al. [14] and Rybina et al. [15] have investigated the lattice dynamical properties of LuB_{12} . Low temperature properties and superconductivity of LuB_{12} compound have been studied by Flachbart et al. [16]. The electronic structure and chemical bonding have been analyzed from partial densities of states and electron densities by Jager et al. [17]. The heat capacity and dilatation of LuB_{12} have been studied by Czopnik et al. [18]. Teyssier et al. [19] have reported a detailed study of specific heat, electrical resistivity, and optical spectroscopy for this compound. Czopnik et al. [18] have studied the thermal expansion and heat capacity of lutetium dodecaborides.

In the present paper, we aim to investigate the structural, elastic, and lattice dynamical properties of LuB_2 , LuB_4 , and LuB_{12} compounds in detail and interpret the salient results of our calculations. The method of calculation is given in Section 2; the results are dis-

* Corresponding author. Tel.: +90 382 2801232; fax: +90 382 2801246.

E-mail address: edeligoz@yahoo.com (E. Deligoz).

Table 1
Crystallographic atomic positions for LuB₂, LuB₄, and LuB₁₂.

Materials	Structure	Space group	Atom	Site	Internal parameters		
					x	y	z
LuB ₂	Hexagonal	191 (<i>P6/mmm</i>)	Lu	1a (0, 0, 0)			
			B	2d (1/3, 2/3, 1/2)			
			Lu	4g (<i>x</i> , <i>x</i> + 1/2, 0)	0.3195		
LuB ₄	Tetragonal	127 (<i>P4/mbm</i>)	B(1)	4e (0, 0, <i>z</i>)			0.2022
			B(2)	4h (<i>x</i> , <i>x</i> + 1/2, 1/2)	0.0865		
			B(3)	8j (<i>x</i> , <i>y</i> , 1/2)	0.1772	0.0387	
LuB ₁₂	Cubic	225 (<i>Fm-3m</i>)	Lu	4a (0, 0, 0)			
			B	48i (−1/2 − 2 <i>y</i>), 1/2, 1/2)		0.6691	

cussed in Section 3. Finally, the summary and conclusion are given in Section 4.

2. Method of calculation

In the present paper, all calculations have been carried out using the Vienna ab-initio simulation package (VASP) [25–30] based on the density functional theory (DFT). The electron-ion interaction was considered in the form of the projector-augmented-wave (PAW) method with plane wave up to energy of 450 eV [27,29]. This cut-off was found to be adequate for studying the structural and lattice dynamical properties. We have not observed statistically significant changes in the key parameters when the energy cut-off is increased from 450 to 650 eV. For the exchange and correlation terms in the electron–electron interaction, Perdew–Burke–Ernzerhof (PBE) type functional [30] was used within the generalized gradient approximation (GGA). For k-space summation the $11 \times 11 \times 11$ for LuB₂ and $8 \times 8 \times 8$ for LuB₄ and LuB₁₂ Monkhorst and Pack [31] grid of k-points have been used.

3. Results and discussion

3.1. Structural properties

For LuB_x structures, which are LuB₂ (*P6/mmm* (space group: 191)), LuB₄ (*P4/mbm* (space group: 127)), and LuB₁₂ (*Fm-3m* (space group: 225)), are considered. All parameters and crystallographic atomic positions for LuB₂, LuB₄, and LuB₁₂ are given in Table 1. The bulk moduli and its pressure derivative have been computed minimizing the crystal total energy for different values of the lattice constant by means of Murnaghan's equation of state [32] as in Fig. 1. From Fig. 1, it can be clearly seen that the tetragonal struc-

ture (*P4/mbm*) is the most stable phase among the three different crystal phases.

The calculated lattice parameters, bulk modulus, the pressure derivative of bulk modulus, and bond distances are listed in Table 2f along with the available experimental and theoretical values for LuB₂, LuB₄, and LuB₁₂. It is seen that the present lattice parameters, bulk modulus are in good agreement with the theoretical and experimental values. In the present case, the largest value of bulk modulus (218.1 GPa) is obtained for LuB₁₂. The calculated bond lengths of LuB₁₂ are consistent with the theoretical data [14]. Unfortunately, there are no experimental and theoretical data for the comparison bond lengths of the other compounds.

3.2. Elastic properties

The elastic constants of solids provide a link between mechanical and dynamical behavior of crystals, and give important information concerning the nature of the forces operating in solids. In particular, they provide information on the stability and stiffness of materials, and their ab-initio calculations require precise methods. Since the forces and the elastic constants are functions of the first-order and second-order derivatives of the potentials, their calculation will provide a further check on the accuracy of the calculation of forces in solids. They also provide valuable data for developing inter atomic potentials. Also, many physical properties of solids depend on their phonon properties, such as specific heat, thermal expansion, heat conduction, and electron-phonon coupling.

We have used the “stress-strain” relations to compute the elastic constants [33], and the findings are given in Table 2. Unfortunately, there are no theoretical or experimental results except for LuB₁₂ compound for comparing with the present work. Then, our results can serve as a prediction for future investigations. *C*₁₁ are in agreement with the experimental value [13], but *C*₁₂ and *C*₄₄ are lower (about 10%) than experimental value (see Table 3) for LuB₁₂. The calculated eigenvalues of the elastic constants matrix are all positive, which confirms that LuB₂, LuB₄, and LuB₁₂ are mechanically stable.

The elastic constants *C*₁₁ or *C*₃₃ measure the *a*- or *c*-direction resistance to linear compression, respectively. The present *C*₁₁ is higher than the *C*₃₃ for LuB₂ and LuB₄. Thus, the *c* axis is more compressible than the *a* axis. It is known that the elastic constant *C*₄₄ is the most important parameter indirectly governing the indentation hardness of a material. The large *C*₄₄ means a strong ability of resisting the monoclinic shear distortion in (100) plane, and the *C*₆₆ relates to the resistance to shear in the (110) direction. In the present case, *C*₄₄ for LuB₁₂ and *C*₆₆ of LuB₂ are higher than those of the other compounds.

The Poisson's ratio (*ν*), shear modulus (*G*), and Young's modulus (*E*), which are the most interesting elastic properties for applications, are often measured for polycrystalline materials while investigating their hardness. These quantities have been calculated

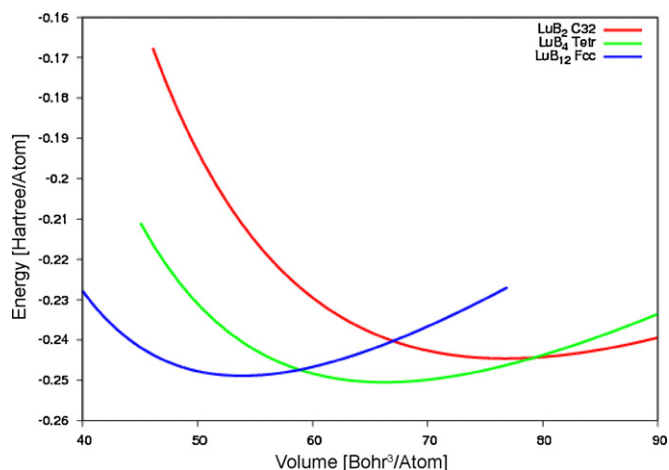


Fig. 1. Energy versus volume curves.

Table 2

Calculated equilibrium lattice parameters (a , b , and c in Å), bulk modulus (B), the pressure derivative of bulk modulus (B'), and the Lu–Lu, Lu–B, and B–B bond distance (in Å) along with the available experimental value for LuB₂, LuB₄, and LuB₁₂.

Materials	Structure	Space group	a	c	B	B'	Lu–Lu	Lu–B	B–B
LuB ₂	Hexagonal	191 ($P6/mmm$)	3.242	3.717	166.9	3.411	3.242	2.615	1.872
	Experimental ¹¹		3.284	3.704					
	Experimental ¹⁹		3.246	3.704					
LuB ₄	Tetragonal	127 ($P4/mbm$)	7.028	3.971	183.5		3.589	2.701	1.606
	Experimental ²⁰		6.997	3.938					
LuB ₁₂	Cubic	225 ($Fm-3m$)	7.457		218.3	3.518	5.272	2.771	1.783
	Experimental ¹³		7.464		232				
	Experimental ¹⁹		7.422						
	Theory ¹³		7.413		223				
	Theory ¹⁴								
	Theory ¹⁷		7.455				5.28	2.78	1.76

Table 3

Calculated elastic constants (in GPa), Poisson's ratio (ν), Young's modulus (E , in GPa), isotropic shear modulus (G , in GPa), bulk modulus (B , in GPa), hardness (H , in GPa) and Debye Temperature (Θ_D , in K) along with the available experimental values for LuB₂, LuB₄, and LuB₁₂.

Materials	Structure	Space Group	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B	G	E	ν	H	Θ_D
LuB ₂	Hexagonal	191 ($P6/mmm$)	441.5	40.8	75.6	362.4	176.4	200.3	180.7	179.7	404.8	0.126	17.33	627.9
LuB ₄	Tetragonal	127 ($P4/mbm$)	485.3	69.2	31.8	444.1	119.0	149.5	186.1	109.7	275.2	0.200	50.52	595.4
LuB ₁₂	Cubic	225 ($Fm-3m$)	449.6	108.2			262.1		222.0	220.6	497.1	0.128	48.23	1097.9
	Experimental ¹³		450	123			290		232			0.215		1110

in terms of the computed data by using the relation given in Ref. [34]. The calculated Poisson's ratio, Young's modulus, bulk modulus, and isotropic shear modulus are given in Table 3. The value of the Poisson's ratio is indicative of the degree of directionality of the covalent bonds. The value of the Poisson's ratio is small ($\nu=0.1$) for covalent materials, whereas for ionic materials a typical value of ν is 0.25 [35].

The LuB₄ has the largest Poisson's ratio, but LuB₂ and LuB₁₂ compounds have the smallest one for these compounds. The calculated Poisson's ratio is about 0.12 for LuB₂ and LuB₁₂ compounds, therefore, there is higher covalent contribution in inter-atomic bonding for these compounds.

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. When the value of E is large, the material is stiff. On this context, due to the higher value of Young's modulus (497 GPa) LuB₁₂ is relatively stiffer in LuB₁₂. If the value of E , which has an impact on the ductility, increases, the covalent nature of the material also increases. From Table 3, one can see that E increases when as we move across LuB₂ \rightarrow LuB₄ \rightarrow LuB₁₂.

Among the bulk and shear moduli in Table 3 calculated with the Voigt–Reuss–Hill approximation [36], the largest value of isotropic shear modulus (220.6 GPa) is obtained for LuB₁₂. According to criterion [37,38], a material is brittle (ductility) if the B/G ratio is less (high) than 1.75. The value of the B/G is less than 1.75 for LuB₂, LuB₄, and LuB₁₂; hence, these compounds will behave in a brittle manner. Moreover, for covalent and ionic materials the typical relations between bulk and shear modulus are $G \approx 1.1B$ and $G \approx 0.8B$, respectively [35]. The present value of $G/B \approx 1.0$ strongly supports the covalent contribution to inter atomic bonding in LuB₂ and LuB₁₂ compounds.

We have calculated the hardness of the LuB₂, LuB₄, and LuB₁₂ compounds by using a semi empirical method which was developed by Simunek and Vackar [39,40]. The method is based on the atomic properties and strengths. Recently, the hardness of ReB₂, MnB₂, and TcB₂ has been successfully predicted by Aydin and Simsek [41]. In the present study, some used data for the hardness calculations were taken from [40,42]. Surprisingly, our results given in Table 3 show that these compounds except to LuB₂ are superhard ($H \geq 40$ GPa) materials, and LuB₄ is hardness one among them. It is interesting that though the shear modulus and Young's modulus

of LuB₄ are lower than those obtained for LuB₂, LuB₁₂, but LuB₄ is harder than the others.

The Debye temperature is known as an important fundamental parameter closely related to many physical properties such as specific heat and melting temperature. At low temperatures the vibrational excitations arise solely from acoustic vibrations. Hence, at low temperatures the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements. We have calculated the Debye temperature by using the common relation given in Ref. [43]. The calculated values of the Debye temperature are given in Table 3. The LuB₁₂ compound possesses the largest Debye temperature (1097.9 K) among the other phases and this value is in agreement with the experimental value in [13].

3.3. Lattice dynamical properties

The phonon dispersion curves and phonon density of state of LuB₂, LuB₄, and LuB₁₂ are calculated by using the Phonon software [44,45] in a manner similar to our recent works [46–48]. The obtained phonon dispersion curves and the corresponding one-phonon DOS for LuB₂, LuB₄, and LuB₁₂ along the high-symmetry directions are illustrated in Figs. 2–4. Unfortunately, there are no other theoretical or experimental results for comparing with the present work except for LuB₁₂. The Γ point frequencies of LuB₁₂ compound are in general, favorable agreement with the other works [20,21].

The calculated phonon dispersion curves have no soft mode at any vectors, which confirms the stability of LuB₂, LuB₄, and LuB₁₂. It can be seen from Figs. 2–4 that the mass difference between anions and cations significantly affects the shapes of the dispersion curves and the corresponding density of states. The mass difference is larger for these compounds, and hence the divergences between the acoustic and optical branches are very clear. Interesting features of optical phonon modes are observed at Γ point. Optical phonon branches are nearly flat at the Γ point and a clear gap is formed between optical branches except for LuB₂ for these compounds, except LuB₄. Acoustic phonon modes include atomic vibrations from both Lu and B atoms. Due to the mass difference between Lu and B atoms, the optical modes contain only vibrations of B atom.

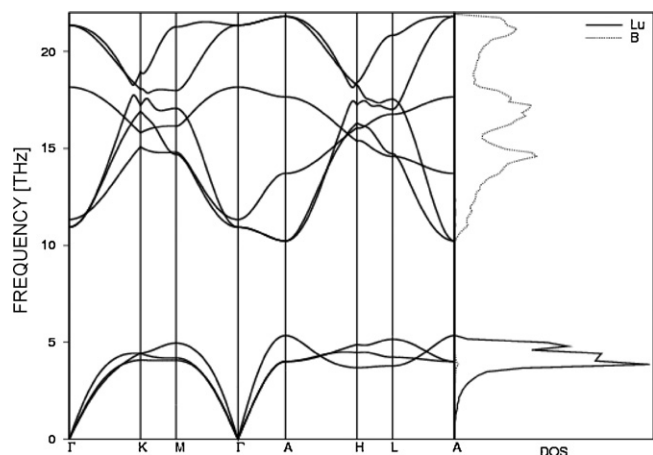


Fig. 2. Calculated phonon dispersions and partial density of states for LuB_2 .

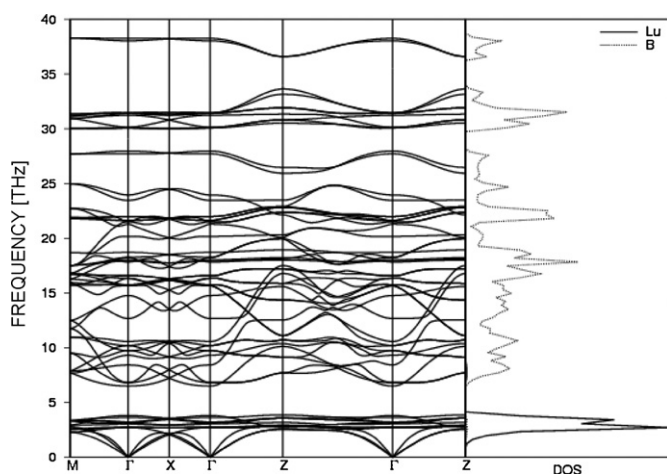


Fig. 3. Calculated phonon dispersions and partial density of states for LuB_4 .

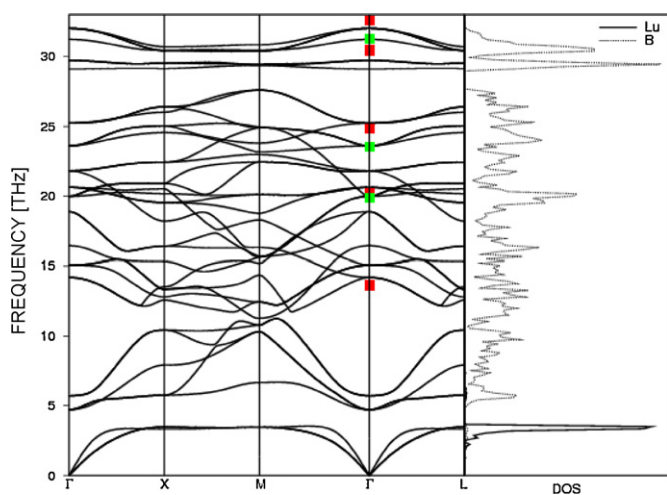


Fig. 4. Calculated phonon dispersions and partial density of states with the experimental Γ point frequencies (■, ■) for LuB_{12} .

On the right side of phonon curves, the corresponding partial density of phonon states are plotted for these compounds. While it is observed that the main contribution to acoustic phonons comes from the Lu atoms sublattice, the high-frequency phonons stem from the boron ions. This is expected because the boron atom is lighter than Lu atoms. The covalent character of the B–B bonding

is decisive for the high frequency of phonons involving the boron atoms.

4. Summary and conclusion

The presented results on the several ground states, structural, elastic, mechanical and vibrational properties for LuB_2 , LuB_4 , and LuB_{12} compounds are obtained using the first-principles calculations implemented in VASP within the GGA. The original aspects of the present calculations concern the elastic properties, mechanical results, and phonon dispersion curves, which are not considered previously, except for LuB_{12} . The calculated phonon dispersion curves have no soft mode at any vectors, which confirms the stability of LuB_2 , LuB_4 , and LuB_{12} . We have predicted that LuB_4 and LuB_{12} compounds are potential superhard materials. Consequently, we conclude that our theoretical predictions on the considered properties of LuB_2 , LuB_4 , and LuB_{12} compounds would be serving as a reliable reference for the future experimental and theoretical studies.

Acknowledgment

This work is supported by Gazi University Research-Project Unit under Project No: 05/2009-55.

References

- [1] R.B. Kaner, J.J. Gilman, S.H. Tolbert, *Mater. Sci.* 308 (2005) 1268.
- [2] W. Zhou, H. Wu, T. Yildirim, *Phys. Rev. B* 76 (2007) 184113.
- [3] H.Y. Chung, M.B. Weinberger, J. Yang, S.H. Tolbert, R.B. Kaner, *Appl. Phys. Lett.* 92 (2008) 261904.
- [4] K.E. Spear, Phase behaviour and related properties of rare-earth borides, in: A.M. Alper (Ed.), *Phase Diagrams, Materials Science, and Technology*, vol. 4: The Use of Phase Diagrams in Technical Materials, 1976, p. 91.
- [5] V.V. Novikov, A.V. Matovnikov, *Inorg. Mater.* 44 (2008) 134.
- [6] T. Mori, in: K.A. Gschneidner Jr, J.-C. Bunzli, V. Pecharsky (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, 38, Amsterdam, North-Holland, 2008, p. 105.
- [7] B.T. Matthias, T.H. Geballe, K. Andres, E. Corenzwit, G.W. Hull, J.P. Maita, *Science* 159 (1968) 530.
- [8] J. Etourneau, *J. Less Common Met.* 110 (1985) 267.
- [9] D. Gignoux, D. Schmitt, in: K.H.J. Buschow (Ed.), *Handbook of Magnetic Materials*, 10, Amsterdam, North-Holland, 1997, p. 239.
- [10] K.H.J. Buschow, *Boron and Refractory Borides*, 494, Heidelberg, Berlin, 1977.
- [11] A.V. Matovnikov, V.S. Urbanovich, T.A. Chukina, A.A. Sidorov, V.V. Novikov, *Inorg. Mater.* 45 (2009) 366.
- [12] T. Mori, T. Takimoto, A. Leithe-Jasper, R. Cardoso-Gil, W. Schnelle, G. Auffermann, H. Rosner, Yu. Grin, *Phys. Rev. B* 79 (2009) 104418.
- [13] G.E. Grechnev, A.E. Baranovskiy, V.D. Fil, T.V. Ignatova, I.G. Kolobov, A.V. Logosha, *Low. Temp. Phys.* 34 (2008) 921.
- [14] K.S. Nemkovski, P.A. Alekseev, J.-M. Mignot, A.V. Rybina, F. Iga, T. Takabatake, N.Yu. Shitsevalova, Yu.B. Paderno, V.N. Lazukov, E.V. Nefeodova, N.N. Tiden, I.P. Sadikov, *J. Solid. State. Chem.* 179 (2006) 2895.
- [15] A.V. Rybina, P.A. Alekseev, J.M. Mignot, E.V. Nefeodova, K.S. Nemkovski, R.I. Bewley, N. Yu Shitsevalova, B. Yu, F. Paderno, T. Iga, Takabatake, *J. Phys.: Conference Series* 92 (2007) 012074.
- [16] K. Flachbart, S. Gabani, K. Gloos, M. Meissner, M. Opel, Y. Paderno, V. Pavlik, P. Samuely, E. Schuberth, N. Shitsevalova, K. Siemensmeyer, P. Szabo, *J. Low. Temp. Phys.* 140 (2005) 339.
- [17] B. Jager, S. Paluch, O.J. Zoga, W. Wolf, P. Herzig, V.B. Filippov, N. Shitsevalova, Y. Paderno, *J. Phys.: Condens. Matter* 18 (2006) 2525.
- [18] A. Czopnik, N. Shitsevalova, V. Pluzhnikov, A. Krivchikov, Y. Paderno, Y. Onuki, *J. Phys.: Condens. Matter* 17 (2005) 5971.
- [19] J. Teyssier, R. Lortz, A. Petrovic, D. van der Marel, V. Filippov, N. Shitsevalova, *Phys. Rev. B* 78 (2008) 134504.
- [20] Y. Fujita, N. Ogita, N. Shimizu, F. Iga, T. Takabatake, M. Udagawa, *J. Phys. Soc. Jpn.* 68 (1999) 4051.
- [21] H. Werheit, Y. Paderno, V. Filippov, V. Paderno, U. Schwartz, A. Pietraszko, in: V.V. Skorokhod (Ed.), *Proc. Conf. on Materials and Coatings for Extreme Performances: Investigations Applications Ecologically Safe Technologies for their Production and Utilization*, IPMS, Kiev, 2004, p. 520.
- [22] M. Przybylska, A.H. Reddoch, G.J. Ritter, *J. Am. Chem. Soc.* 85 (1963) 407.
- [23] H. Oesterreicher, K. Oesterreicher, in: H.P.J. Wijn, (Ed.), *Springer Materials-The Landolt-Börnstein Database*.
- [24] O.D. McMasters, K.A. Gschneidner, *Nucl. Metallurgy* 10 (1964) 93.
- [25] G. Kresse, J. Hafner, *Phys. Rev. B* 47 (1994) 558.
- [26] G. Kresse, J. Furthmüller, *Comp. Mater. Sci.* 6 (1996) 15.
- [27] G. Kresse, D. Joubert, *Phys. Rev. B* 59 (1999) 1758.

- [28] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
- [29] P.E. Blochl, Phys. Rev. B 50 (1994) 17953.
- [30] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [31] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048.
- [32] F.D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. 30 (1944) 5390.
- [33] Y.L. Page, P. Saxe, Phys. Rev. B 63 (2001) 174103.
- [34] G.E. Dieter, Mechanical metallurgy Si Metric edition, McGraw-Hill, 1988.
- [35] V.V. Bannikov, I.R. Shein, A.L. Ivanovskii, Phys. Stat. Sol. (RRL) 3 (2007) 89.
- [36] R. Hill, Proc. Phys. Soc. London 65 (1952) 349.
- [37] I.R. Shein, A.L. Ivanovskii, J. Phys.: Condens. Matter 20 (2008) 415218.
- [38] S.F. Pugh, Phil. Mag. 45 (1954) 833.
- [39] A. Simunek, J. Vackar, Phys. Rev. Lett. 96 (2006) 085501.
- [40] A. Simunek, Phys. Rev. B 75 (2007) 172108.
- [41] S. Aydin, M. Simsek, Phys. Rev. B 80 (2009) 134107.
- [42] W.B. Pearson, The Crystal Chemistry and Physics of Metals and Alloys, Wiley, New York, 1972, p151.
- [43] I. Johnston, G. Keeler, R. Rollins, S. Spicklemire, Solid State Physics Simulations, The Consortium for Upper-Level Physics Software, John Wiley, New York, 1996.
- [44] K. Parlinski, Software, PHONON, 2003, and references therein.
- [45] K. Parlinski, Z.Q. Li, Y. Kawazoe, Phys. Rev. Lett. 78 (1997) 4063.
- [46] E. Deligöz, K. Çolakoğlu, Y.Ö. Çiftçi, Solid State Commun. 149 (2009) 1843.
- [47] E. Deligöz, K. Çolakoğlu, Y.Ö. Çiftçi, Solid State Commun. 150 (2010) 405.
- [48] E. Deligöz, K. Çolakoğlu, Y.Ö. Çiftçi, Comp. Mater. Sci. 47 (2010) 875.