Theoretical study of some materials used in refrigeration systems

Saber Saad essaoud[1], Zoulikha Charifi [2] and Hakim Baaziz[2]

[1] Laboratoire de Physique des Particules et Physique Statistique, Ecole Normale Supérieure Vieux Kouba, Alger-Algérie.

[2] Physics Department, Faculty of Science, University of M'sila.
Corresponding author: e-mail Saber-ss1986@hotmail.com

Résumé *:* Récemment, les composés MnBi et MnSb sont parmi les matériaux utilisés pour produire des équipements de réfrigération. Cependant, les scientifiques ont effectué plusieurs études théoriques et des expérimentations afin d'étudier les propriétés structurales, électroniques, magnétiques et élastiques. Dans notre travail, nous avons étudié les propriétés structurales, électroniques, magnétiques et élastiques de MnBi et MnSb en utilisant la méthode FP-LAPW dans le cadre de la théorie de la fonctionnelle de la densité (DFT). Le terme du potentiel d'échange et de corrélation a été traité par deux différentes approximations LDA et GGA. Pour les Propriétés structurales, nous avons calculé les paramètres de la maille, le module de compressibilité. D'autre part, nous avons calculé la structure de bandes, la densité d'états totale et partielle et de la densité de charge et comparé les résultats obtenus avec d'autres calculs théoriques et expérimentales. On a calculé aussi le moment magnétique total et le moment magnétique de l'atome de manganèse. Enfin, on a défini aussi quelques paramètres élastiques comme le module de Young (E), le facteur d'anisotropie (A), le module de compressibilité adiabatique (Bs) et le module de cisaillement (G déformation résistance). La stabilité mécanique de ces matériaux a été traitée et exprimée a travers les constantes élastiques.

Mots clés : DFT, FP-LAPW, MnBi, MnSb, les constants élastiques, half-metal.

Nomenclature :

R_{MT}: le r*ayon* moyen *de* la *sphère* de muffin-tin

Kmax: la valeur maximale du vecteur d'onde

B: le module de compressibilité

E : le module de Young

A : le facteur d'anisotropie

Bs: le module de compressibilité adiabatique

G : le module de cisaillement.

C_{11} : élasticité de la longueur

C_{44} : élasticité de la forme

1. Introduction:

Since discovering the magneto-caloric effect (EMC) by E.Warburg [1], several researches departed about the properties of materials which can realized this effect, In our work we look for the structural, electronic, magnetic and elastic properties of MnBi and MnSb zinc-blende phase by using the density functional theory (DFT) [2-3] within FP-LAPW[4] method, the exchange-correlation term is treated using two approximations LDA [5] (local density approximation) and GGA [6] (generalized gradient approximation).

This paper is organized as follows: in section 2, we describe the crystal structures of MnBi and MnSb, and we give some computation details. Section 3 is devoted to the discussion and analysis of the obtained results. Finally, we summarize the obtained results in section 4.

2. Computational details:

Both compounds MnBi and MnSb have the zinc-blende structure with F-34m (216) space group. The lattice constants are a = $6.39A^0$, $6.166A^0$ for MnBi and MnSb respectively. Mn is in (0 0 0) position and the other atom (Bi or Sb) takes the position (1/4 1/4 1/4).

Our calculation based on FP-LAPW method implemented in Wien2k code [7]. We used local density approximation (LDA) and generalized gradient approximation (GGA) to treat the exchange-correlation potential. We select the Rmt*Kmax equal to 9, and The R_{MT} are taken to be 2, 2, 2, 2.5 and 2.4 atomic units for Mn, Sb and Bi respectively. The electronic configurations (for valence electrons) are for Mn: $3P^6\ 3d^5\ 4S^2$**,** for Bi: $4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$, and for Sb: $3d^{10}\ 4s^2\ 4p^3$.

3. Main calculated results

At the beginning we present the structural properties, so, we define the equilibrium lattice constants via plotting the total energy variation for each phase as function of volume for the two compounds with LSDA and GGA approximations. Our calculation results are summarized in Table.1 and compared with other theoretical calculations. In fig.1, the calculated energies using GGA approximation are presented. From table.1 it is clearly seen that GGA approximation give a good results than those of LDA ones.

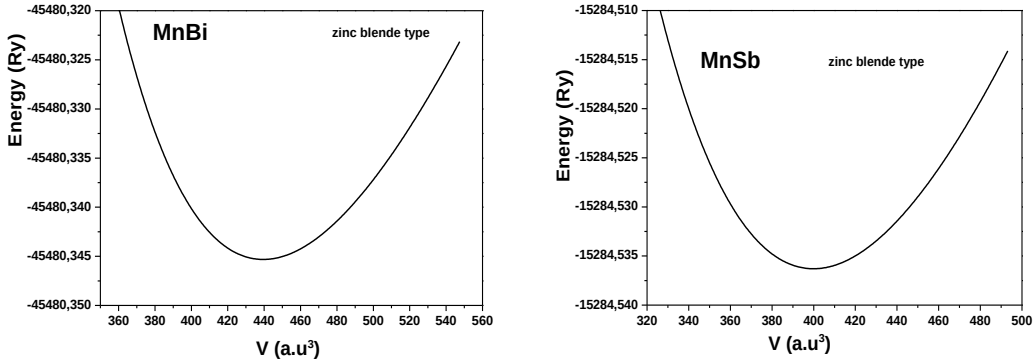


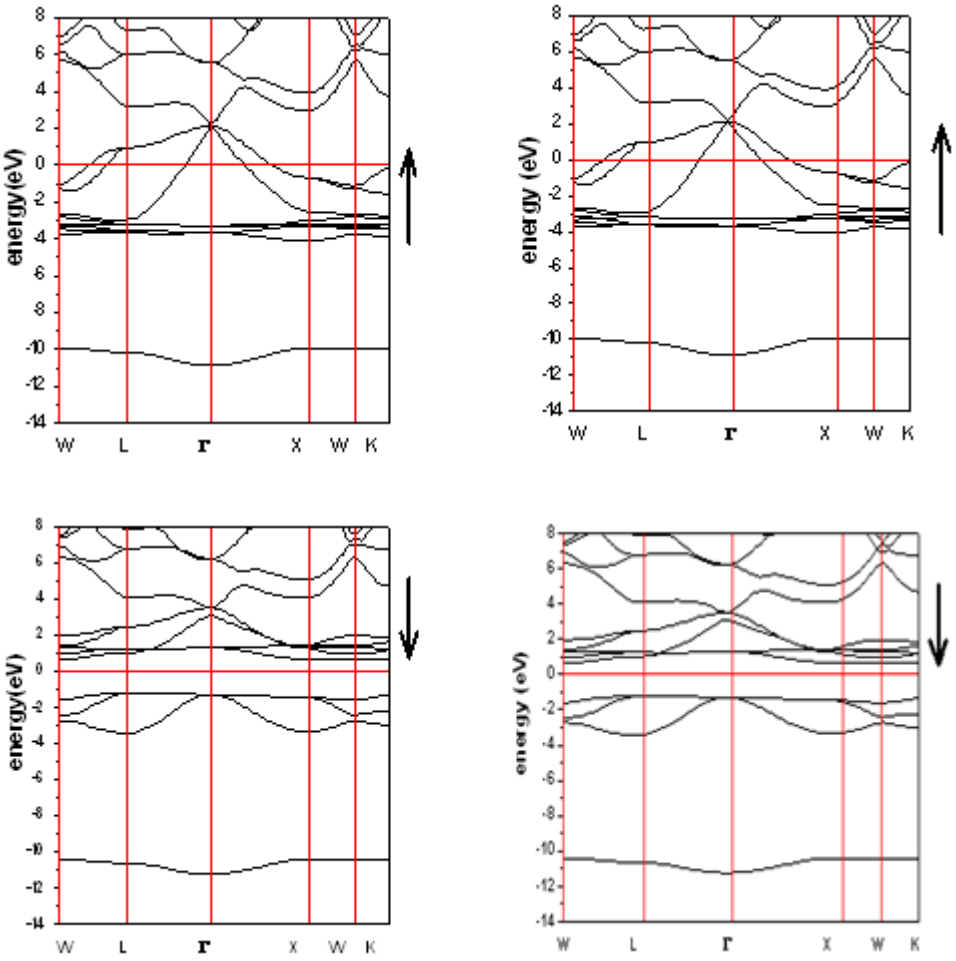
Figure.1: Variation of total energy as function as volume for zinc-blende phase for MnBi and MnSb.

The second step in this work is the study of the electronic properties so we discuss the band structure and DOS of MnBi and MnSb compounds calculated using MBJ (modified Becke-Johnson exchange potential Approximation for treating the exchange correlation term). For the band structure, figure.2 shows that MnBi in zinc blende phase and at its equilibrium lattice constant behaves as a half metallic and it is clear that spin up electrons, MnBi is a metallic, but in spin it

behaves like a semiconductor with energy gap about 1.3ev. We can see also the same remark for MnSb with a gap equals to 1.5 ev for spin down.

Table.1: Equilibrium lattice constants, Bulk moduli and magnetic moment with SLDA and GGA for MnBi and MnSb in zinc-blende type structure.

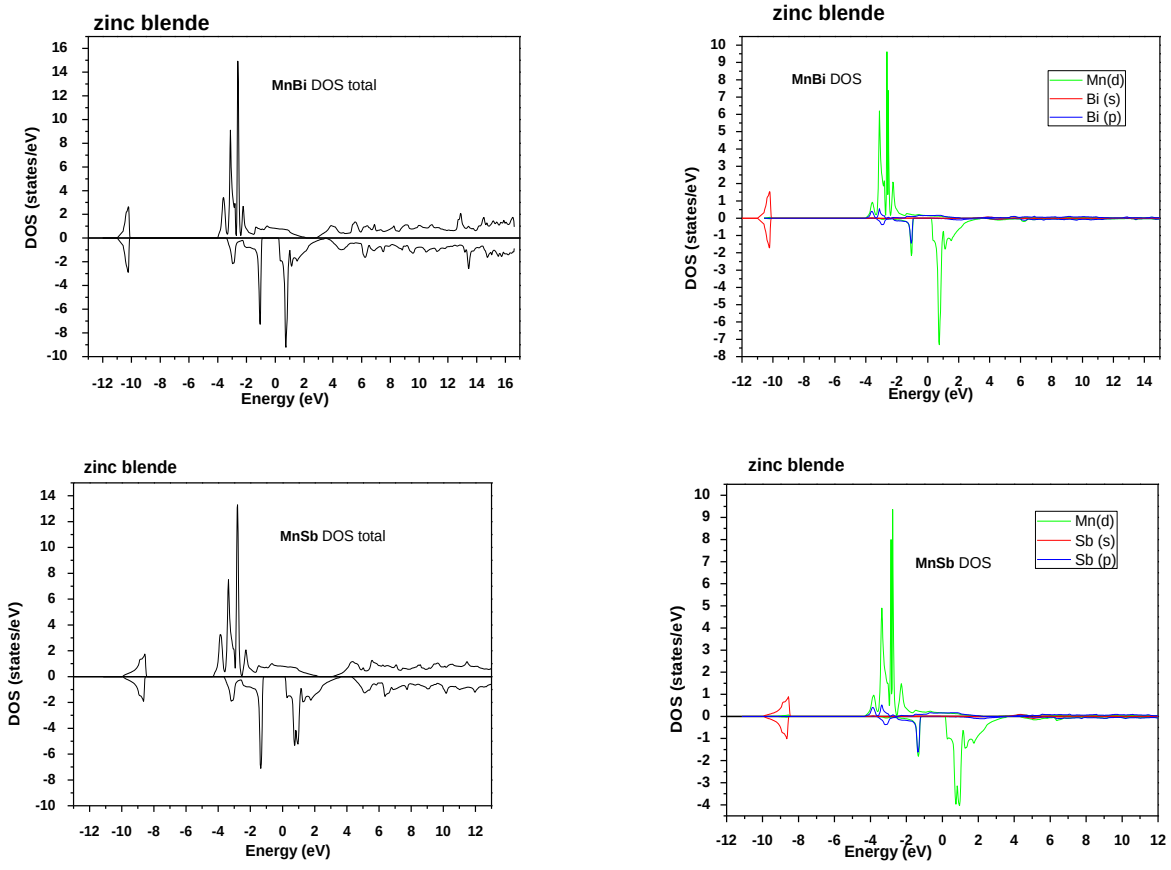
	MnBi			MnSb		
	B(GPa)	a (A^0)	magnetic moments (μ_b)	B(GPa)	a (A^0)	magnetic moments (μ_b)
LSDA	43.2364	6.1459	(Mn) 3.08879	46.5968	5.9314	(Mn) 3.83746
			(Bi) -0.07580			(Sb) -0.16041
			Tot 3.35672			Tot 4.00125
GGA	36.5581	6.3869	(Mn) 3.70350	41.2096	6.1890	(Mn) 3.62224
			(Bi) -0.12417			(Sb) -0.12068
			Tot 4.00196			Tot 3.98762
Other works	/	6.346[8]	Tot 4.000[9]	/	6.166[10]	Tot 3.77[9]



MnBi MnSb

Figure .2: band structures for MnBi and MnSb in zinc-blende type structure calculated using MBJ (modified Becke-Johnson exchange potential) approximation.

Figure.3 present the corresponding spin dependent density of states for both compounds MnBi and MnSb calculated at the equlibruim constant in zinc blende phase. we can see for both cases of spin an energy band take place between (-12ev, -10ev) for MnBi and it contained (6s) states of Bi atom contribution . For MnSb this band was in the range (-10ev, -8ev) and it contained the contribution of (4s) states of Sb atom. Also, for spin up, the hybridization of (3d) states of Mn atom with the (6p) of Bi atom formed the contribution band. In case of MnSb compound we see the same observation and the hybrzidation was happened between (3d) states of Mn and (4p) states of Sb. The results obtained via studying the band structures and the density of states for both mnBi and MnSb reached us to say that MnBi and MnSb behave in zinc blende phase as a half mettalics.



MnBi MnSb

***Figure .3**: Partial and total density (DOS) for MnBi and MnSb with MBJ method in zinc-blende type structure.*

The contour plots of the electronic density for the valence charges appear that the bonding between atoms is covalent and when we return to the DOS graphes (figure. 3) we deduce that this covalent bonding and electronic density increases in the interstitial region. Finally we can said that this observation about the electronic density confirm and support what we have found in our analysis of the DOS for both compounds.

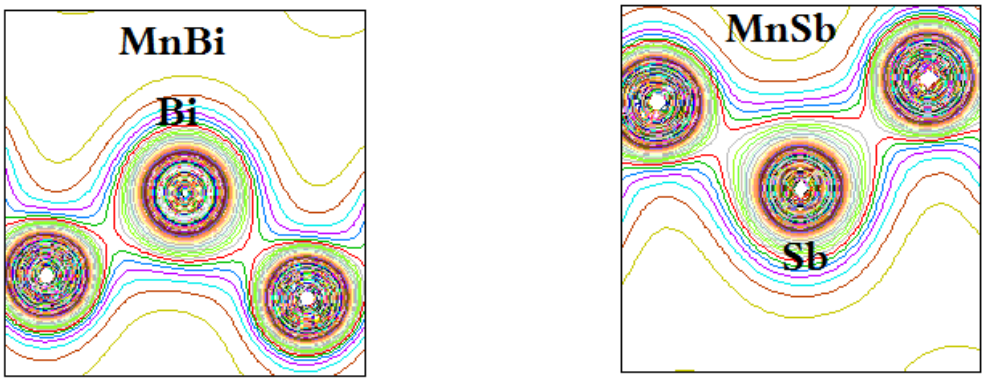


Figure .4: *electronic charge Density for MnBi and MnSb in zinc-blende type structure.*

we present in the end of this work the elastic properties which are summarized in table.4, so we present the elastic constants C11, C12, C44 and Cs , moduli of Young E, theanisotropy factor A and the adiabatic moduli of compressibility Bs and the shear moduli G (deformation resistance). the elastic constants C11, C12, C44 and Cs and each of Bs , G , A and E are given as follow:

$$E = \frac{(C_{11} - C_{12})(C_{11} + 2C_{12})}{C_{11} + C_{12}} \quad (1)$$

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

$$B = \frac{1}{3}\ (C_{11} + 2C_{12}) \quad (3)$$

$$C_s = \frac{1}{2}\ (C_{11} - C_{12}) \quad (4)$$

$$G = \frac{1}{2}\left[\frac{C_{11} - C_{12} + 3C_{44}}{5} + \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})}\right] \quad (5)$$

According to the obtained (table.2), we note the following points:

1- MnBi does not verify the mechanic criterion of stability (C_{11}, C_{12} and C44>0, (C_{11}+2 C_{12}) >0, but (C_{11}- C_{12}) take negative value . also B_s value's is less than C_{12} and greater than C_{11}. The anisotropy factor A is smaller than 1 so we can deduce that this crystal is harder in <1,0,0> direction. Wa calculate also B/G ratio and this factor is a criterion used to know if material have brittle and ductile property: If B/G>1.75, it means that material had a low resistance to shear, hence ductility. In the otherwise, B/G>1.75 means that material had a low resistance fracture, hence brittleness.

2- MnSb compound checked the mechanic conditional of stability (C_{11}, C_{12} and C44>0, (C_{11}-C_{12}) >0, (C_{11}+2 C_{12}) >0, and C_{12}<B_s < C_{11}. For the anisotropy factor A is greater than 1 so we can deduce that this crystal more harder in <1,1,1> direction. We can see also that (B_s/G) is more than 1.75 so, MnSb is a ductile material.

***Table.2**: elastic properties of MnBi and MnSb in zinc-blende type structure.*

	C_{11} (GPa)	C_{12}(GPa)	C_{44}(GPa)	C_s(GPa)	B_s(GPa)	G(GPa)	A(s.u)	E(GPa)	B_s/G
MnBi	14.230	25.068	8.858	-5,419	21.456	-80,677	-1,634	-23,955	-0,265
MnSb	34.203	25.259	23.751	4,472	28.241	12,378	5,311	47,413	2,281

4. Conclusion

Our work of the structural, electronic, magnetic and elastic of MnBi and MnSb by using FPLAPW method lead us to extract several features and properties of these compounds. So, we found for the structural parameters that for both compounds we have obtained results in good agreement with the experimental and the other results,and we have found that for the electronic properties we deduce that MnBi and MnSb are half metallic in zinc blende with no gap energetic for spin up for both compounds and they behave as a semiconductor for pin down with gap 1.3eV and 1.5eV for MnBi and MnSb respectively.

For the elastic properties we find MnBi is a brittle material and it is harder in the direction <1,0,0> and it doen't checked the mechanical stability condition. In the other hand we found that MnSb compound check the mechanical stability condition and it is harder in <1,1,1> direction and we can say MnSb is a ductile material.

References:

[1] E. Warburg, Ann. Phys. 13 (1881) 141.

[2] P. Hohenberg and W.Kohn, Phys. Rev 136, 864 (1964).

[3] L.J.Sham, W.Kohn, Phys. Rev. 145, 561 (1966).

[4] D. R Hamann, Phys. Rev. Lett. 212, (1979) 662.

[5] D. M. Ceperley , B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).

[6] J. P. Perdew, S. Burke et M. Ernzerhof, Phys. Lett. 77, 3865 (1996).

[7]. Blaha, P., Schwarz, K., Madsen, G.K.H., Kvasnicka, D., Luitz,J.: Wien2k, an augmented plane wave plus local orbitals program for calculating crystal properties, Vienna University of Technology, Vienna (2001).

[8]J.P. Perdew, S. Burke, M. Ernzerhof, Phys. Rev. Lett. 77(1996) 3865.

[9]Ya-Qiong Xu, Bang-Gui Liu, D.G. Pettifor elsevier Physica B 329–333 (2003) 1117–1118

[10] San-Dong Guo and Bang-Gui Liu. Cond-mat :mtrl-sci 10 sep 2010.