# Pressure effect on structural, electronic and magnetic properties of the *M*As (*M* = Cr, Mn) binary compounds: A first-principles study

Ahlem kolli
*Department of Physics, Faculty of Science, University Ferhat Abbas Setif 1*
*Laboratory of Surfaces and Interfaces Studies of Solid Materials (L.E.S.I.M.S)*
Setif, Algeria
ahlem.kolli@univ-setif.dz

Nacir Guechi
*Department of Medicine, Faculty of Medicine, University Ferhat Abbas Setif 1*
*Laboratory of Surfaces and Interfaces Studies of Solid Materials (L.E.S.I.M.S)*
Setif, Algeria
nacir_guechi@yahoo.fr

***Abstract*—In this work, we have studied the structural, electronic and magnetic properties of the *M*As (*M* = Cr, Mn) binary compounds in the zinc blende phase, under hydrostatic pressure using ab initio calculations. The spin polarized calculations were performed using the Pseudo-Potential Plane Wave (PP-PW) method based on the Density Functional Theory (DFT) as implemented in the CASTEP code. The exchange correlation effect was treated using the GGA-PBE approximation. Geometric optimizations were performed for a pressure range between -8.5 and 30GPa. The calculated equilibrium lattice constant (*a*) for both compounds agrees very well with the available theoretical and experimental reports. According to the bulk modulus (*B*) values, the CrAs compound with *B* = 64.53 GPa is more resistant to volume changes than the MnAs compound with *B* = 45.98 GPa. The electronic populations, energy band structures and density of states were calculated to determine the magneto-electronic properties. Analysis of the obtained results shows that these compounds exhibit a half-metallic ferromagnetic behavior with a band gap in the minority spin states resulting from the *p-d* hybridization. The total magnetic moment of *M*As compounds comes mainly from the incomplete *d*-orbital of the Cr (Mn) atoms, and it is almost equal to an integer values of 3 $\mu_B$ (4 $\mu_B$) per unit cell which is consistent with the Slater-Pauling rule. the half-metallicity in the studied compounds is generally maintained over a wide pressure range. These results would help in incorporating *M*As (*M* = Cr, Mn) compounds in spintronic devices.**

***Keywords*—DFT, PP-PW, CrAs, MnAs, half-metallicity**

## I. INTRODUCTION

Half-metallic ferromagnets (HMFs) have the potential to play an important role in the continued development of spintronics, which uses electron spins to obtain, transport and process information [1]. The behavior of the HMFs was firstly predicted by de Groot et al. [2] in 1983 based on first-principle calculations for C1b-type Heusler alloys NiMnSb and PtMnSb. These materials behave as metals for one direction of spin and as semiconductors for the other direction of spin, leading to a full spin polarization (100%) at the Fermi level ($E_F$). Half-metallic ferromagnets have attracted much attention because of their high Curie temperature ($T_C$) and large half-metallic band gap [3], among these compounds, MnAs and CrAs.

The transition metal arsenides CrAs and MnAs are part of the large family of transition metal pnictides with a general formula TMX (TM = transition metal, X = P, As, Sb), Which crystallize in several phases depending on the temperature and pressure. At ambient conditions, CrAs crystallizes in MnP-type orthorhombic crystal structure [4], whereas MnAs adopts the hexagonal NiAs-type structure [5]. CrAs, and MnAs in the Wurtzite (WZ) or zinc-blende (ZB) structures have received particular attention because of compatibility with current III–V or II–VI semiconductors technology. Since 2000, Akinaga et al. [6] were found the possibility to fabricate zinc-blende type CrAs using molecular beam epitaxy (MBE) on a GaAs (001) substrate and found ferromagnetism behavior at room temperature with Curie temperature ($T_C$) higher than 400 K, which is in good agreement with theoretical predictions using Monte Carlo simulation and mean field theory [7]. Moreover, ZB-CrAs compound was found experimentally to exhibit a half-metallic ferromagnetic structure with a magnetic moment of 3 $\mu_B$ [6], These results agree well with the theoretical reports [8, 9]. Recently the growth of ZB-MnAs thin films on GaAs [10, 11] and InP [12] substrates by MBE has been reported. On the other hand, Han et all. [13] have studied the electronic and magnetic properties of the bulk, (001) surfaces and (001) interfaces for zinc blende MnAs by means of the full-potential linearized augmented plane-wave (FPLAPW) method from the first-principle calculations. They predicted that the zinc blende MnAs is a nearly half-metallic ferromagnet with 4.00 $\mu_B$ magnetic moment.

The investigation of the pressure effect on materials properties has attracted much attention. In fact, pressure serves as a versatile tool in materials research. In the current work, we present the results of structural, electronic and magnetic properties of the of the *M*As (*M* = Cr, Mn) binary compounds in the zinc blende phase using the first-principle calculations. We also discuss the half-metallic stability under hydrostatic pressure.

## II. COMPUTATIONAL DETAILS

We have performed the first-principle calculations using the pseudo-potential plane-wave method based on density functional theory (DFT) [14] as implemented in the Cambridge Serial Total-Energy Package (CASTEP) [15], to study the structural and magneto-electronic properties of the *M*As (*M* = Cr, Mn) binary compounds in the zinc blende phase. The exchange-correlation potential and the interaction between the atomic core and the valence electrons were described using the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [16] and the ultrasoft pseudo potential [17]. The considered valence states are: Cr: $4s^1\ 3d^5$; Mn: $4s^2\ 3d^5$; As: $3d^{10}\ 4s^2\ 4p^3$. A plane-wave cut-off energy of 380 eV and a 10 × 10 × 10 k-points in the Brillouin zone were applied for the geometry optimization, we have selected 30 × 30 × 30 k-points to catlculate the density of states. The self-consistent field tolerance was set as a total energy difference smaller

than $5\times10^{-6}$ eV/atom, the maximum force was less than 0.01 eV/Å the maximum stress was smaller than 0.02 GPa and the displacement of atoms was less than $5\times10^{-4}$Å.

## III. Results and Discussion

The *M*As (*M* = Cr, Mn) binary compounds crystallize in The zinc-blende structure which is similar to that of ZnS, possesses a cubic lattice in the space group $F\bar{4}3\,m$, No. 216 with two atoms in the primitive unit cell (Fig. 1- b). The atomic positions are as follows [18] : *M* at (0, 0, 0) in Wyckoff coordinates and (1/4, 1/4, 1/4) occupied by the As atom (Fig. 1-a).

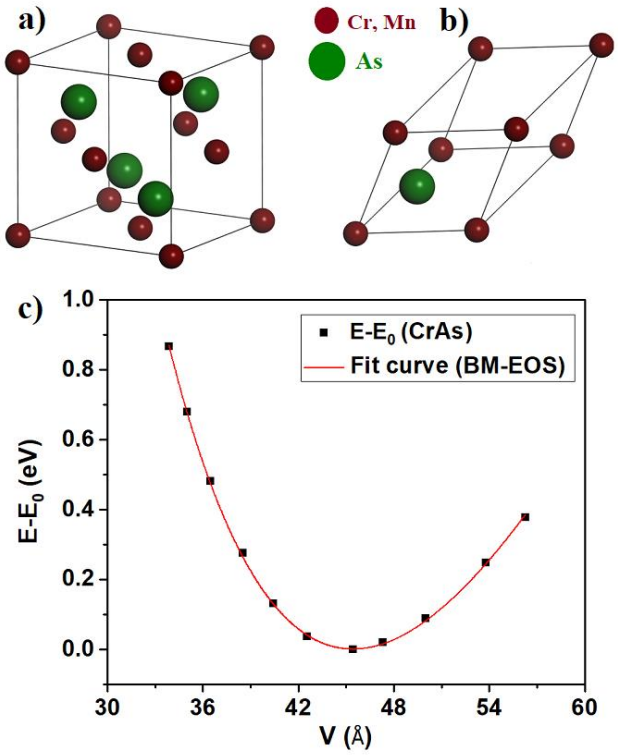


Fig. 1. a) Crystal structure of *M*As (*M* = Cr, Mn) compounds ; b) its corresponding primitive unit cell ; c) Calculated energy as a function of volume of CrAs compound (MnAs have the same curve).

In order to obtain the ground-state parameters, such as the lowest total energy per unit cell ($E_0$), equilibrium lattice constant ($a_0$), equilibrium volume ($V_0$), the bulk modulus ($B_0$) and its derivative ($B$'=d$B$/d$P$), a geometry optimization was performed by computing the total energy of the unit cell at each fixed pressure. The calculated total energy of CrAs compound using GGA-PBE versus unit-cell volume has been fitted to the Birch-Murnaghan (BM) equation of state (EOS) (1) [19] and is displayed in Fig. 1-c.

$$E(V) = E_0 + \left(\frac{9}{16}\right) BV_0 \left( \left(B'-4\right)\left(\frac{V}{V_0}\right)^{\frac{-2}{3}} - B' + 6 \right) \left( \left(\frac{V}{V_0}\right)^{\frac{-2}{3}} - 1 \right)^2 \quad (1)$$

According to the bulk modulus ($B$) values listed in Table I, the CrAs compound with $B$ = 64.53 GPa is more resistant to volume changes than the MnAs compound with $B$ = 45.98 GPa. It is important to note that the obtained results agree very well with the available experimental and theoretical data.

The spin-polarized band structures of *M*As (*M* = Cr, Mn) compounds at different pressures -8.5, 0 and 30 GPa, in the energy range from -4 to 4 eV are given in Fig. 2. At -8.5 and 0GPa, it is clearly seen that the majority spin channel (spin up) exhibits a metallic behavior in which the electronic states belonging to the valence band cross the Fermi level (set at 0 eV), while the minority spin channel (spin down) show a semiconducting nature with an indirect gap of 2.334 and 2.034 eV (1.893 and 1.753 eV) For CrAs (MnAs) compounds at -8.5 and 0 GPa respectively. At these pressures, both compounds can be considered as a perfect half-metallic.

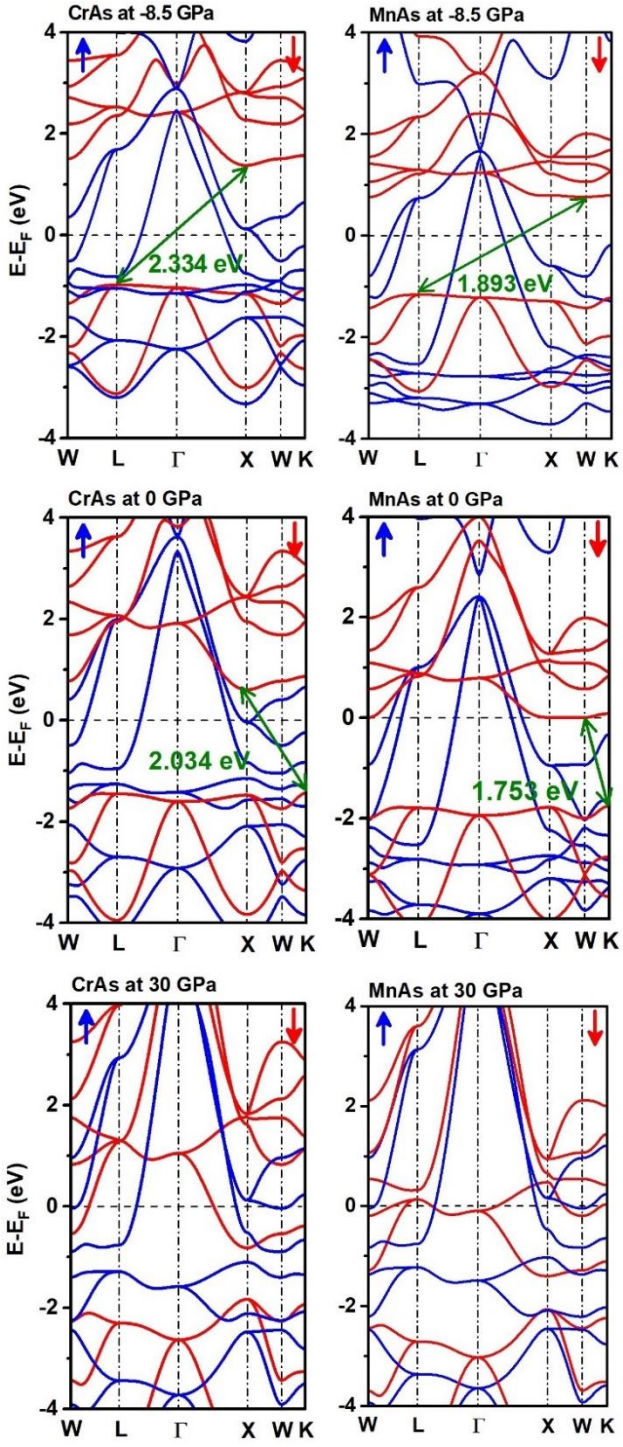


Fig. 2. Band structures for *M*As (*M* = Cr, Mn) compounds at pressures -8.5, 0 and 30 GPa (blue line: spin-up; the red line: spin-down).

However, the compounds at 30 GPa behave totally different, for which the spin majority and the spin minority states exhibit metallic natures.

TABLEI. The calculated lowest total energy per unit cell, $E_0$ (eV), lattice constant, $a_0$ (Å), volume, $V_0$ (Å$^3$), bulk modulus, $B_0$ (GPa) and its derivative $B'$ for the $M$As ($M$ = Cr, Mn).

| | $E_0$ | $a_0$ | $V_0$ | $B_0$ | $B'$ |
|---|---|---|---|---|---|
| CrAs | -2639.7 | 5.663 | 181,69 | 64,53 | 3,13 |
| Expt. [20] | | 5.637 | | | |
| Calc. [7] | | 5.658 | | 67.60 | |
| MnAs | -825.9 | 5,720 | 187,16 | 45,98 | 1.76 |
| Expt. [21] | | 5,689 | | | |
| Calc. [13] | | 5.743 | | | |

The variations of the valence band maximum (VBM) and conduction band minimum (CBM) as functions of hydrostatic pressure from -8.5 to 30 GPa for the spin minority states are shown in Fig. 3. The half-metallic properties of the $M$As ($M$ = Cr, Mn) compounds are maintained in the shaded regions.

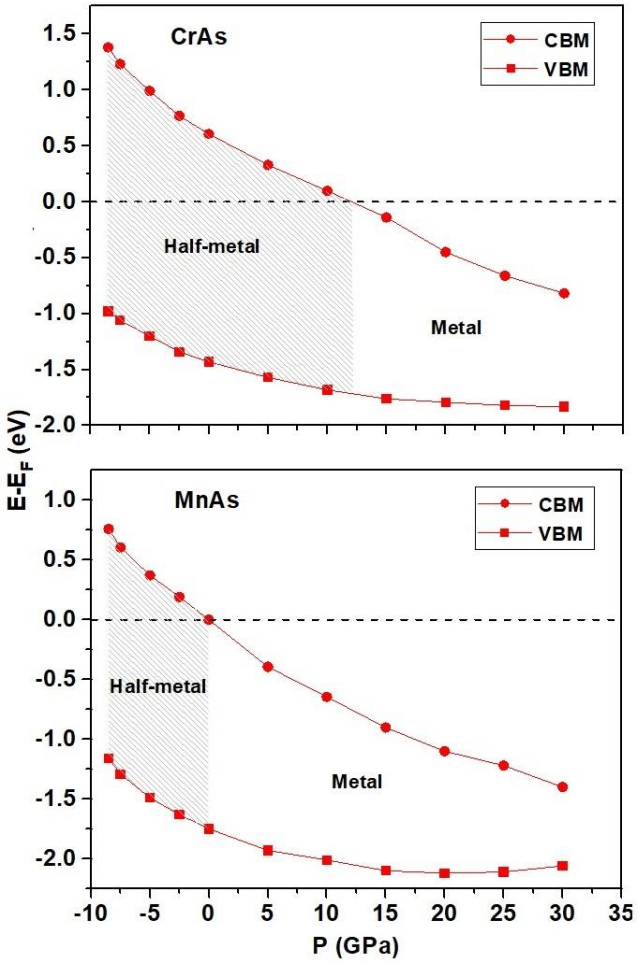


Fig. 3. Valence band maximum (VBM) and conduction band minimum (CBM) of $M$As ($M$ = Cr, Mn) compounds as functions of the hydrostatic pressure.

Increasing the pressure, the VBM and CBM show decreasing trend. For the CrAs and MnAs compounds, the half-metallic regions are -8.50 – 12.17 GPa, -8.5 – 0 GPa, respectively. When CBM crosses the Fermi level, their properties change from the half-metallic character to metallic character. from Fig. 3, we can also see that the half-metallic regions of CrAs compound is more important than that of the MnAs compound.

Further, we investigate with more details the electronic structure of $M$As ($M$ = Cr, Mn) compounds at zero pressure by calculating their total and partial density of states (TDOS and PDOS) in the energy range from -12 to 4 eV, presented in Fig. 4. It is clear to see that the most important contribution around the Fermi level comes essentially from contributions of Cr-3$d$ (Mn-3$d$) states of CrAs (MnAs) compounds, whereas the contribution of 4$p$ states belonging to As atom is small. The lower valence band with energy below −9 eV is due to 4$s$ states of As atom. On the other hand, a clear gap in the minority spin channel is observed for $M$As ($M$ = Cr, Mn)

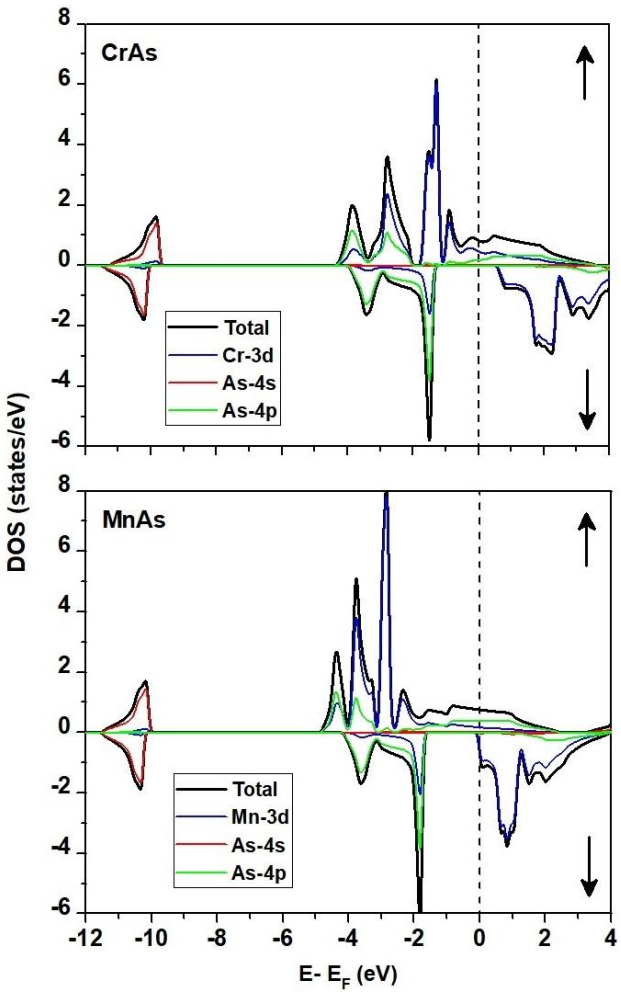


Fig. 4. Total and partial density of states (TDOS and PDOS) at zero pressure.

compounds, the origin of the gap is the sequence of the strong hybridization between the $d$ states around the Fermi level of the transition metal atoms Cr or Mn and the $p$ states of As atom. The calculation of the density of state at zero pressure shows that CrAs and MnAs have a half metallic behavior. These results confirm wath was obtained by studying the band structures and agree very well with theoretical reports [7, 13].

The total and atomic magnetic moments of the *M*As (*M* = Cr, Mn) compounds as a function of the pressure are shown in Fig. 5. In the half-metallic regions, the total magnetic moment is maintained at an integer values of 3 $\mu_B$ (4 $\mu_B$) per unit cell for CrAs (MnAs) compounds and obeys to the "$M_t$=$Z_t$ -8" Slater-Pauling rule [22], where $M_t$ is the total magnetic moment and $Z_t$ is the total number of valence electrons in the unit cell, which is equal to 11 (12) electrons for CrAs (MnAs) compounds. The atomic magnetic moment of Cr, Mn atoms and total magnetic moment decrease, whereas that of As atom increases with increase in pressure, leading to the transition from the half-metallic character to metallic character at pressures greater than 12.17 GPa (0 GPa) for CrAs (MnAs) compounds. As seen in Fig. 5 the main contribution to the total magnetic moment is due to the incomplete *d*-orbital of the Cr or Mn atoms, while the magnetic moment on the As atom is quite small.

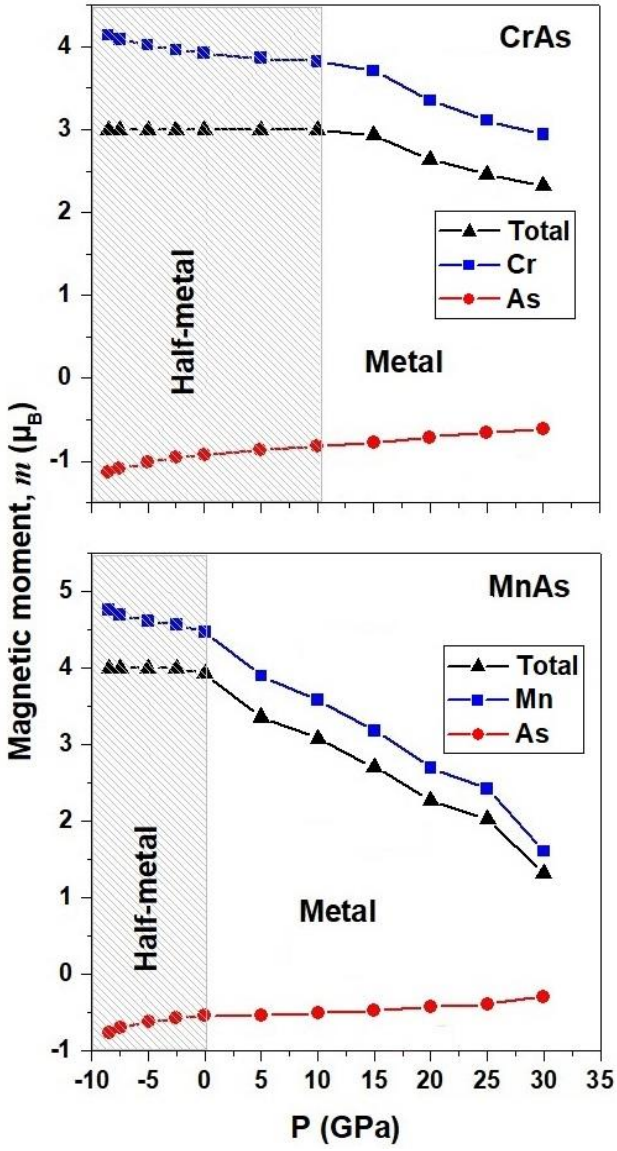


Fig. 5. Variation of the Total and atomic magnetic moments as functions of the hydrostatic pressure.

In Fig. 6, we display the pressure effect on the spin polarization (P) of *M*As (*M* = Cr, Mn) compounds defined by the formula [23] :

$$P = \frac{N\uparrow(E_F) - N\downarrow(E_F)}{N\uparrow(E_F) + N\downarrow(E_F)} \times 100 \quad (2)$$

Where $N\uparrow(E_F)$ and $N\downarrow(E_F)$ are the density of state at Fermi level ($E_F$) in the case of spin-up and spin-down, respectively.

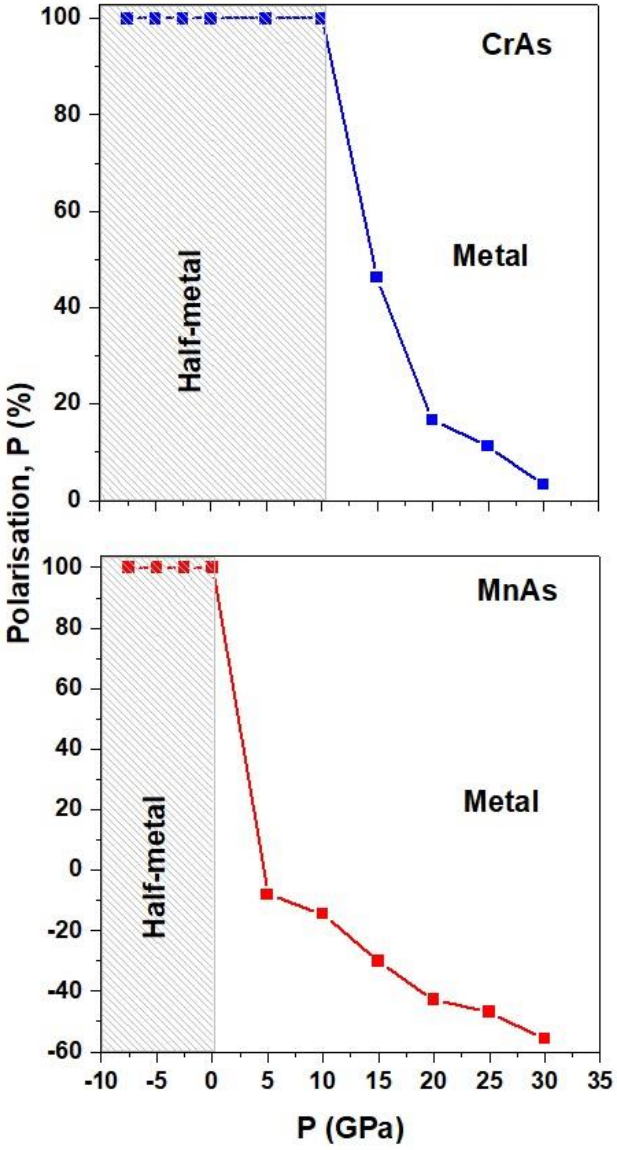


Fig. 6. Variation of the spin polarization (P) as functions of the hydrostatic pressure.

We find that the spin polarization for both compounds in the half-metallic regions is about 100%, which confirm that electrons can participate in conduction in just one spin channel. When the pressure is greater than 12.17 GPa (0 GPa) for CrAs (MnAs) compounds, the spin polarization exhibits a large deviation and rapidly decreases, Thus the compounds acquire a metallic behaviour.

## IV. CONCLUSION

In summary, the effect of hydrostatic pressure on the structural, electronic and magnetic properties of the *M*As (*M* = Cr, Mn) compounds with zinc blende structure have been investigated using the (PP-PW) method with the GGA-PBE approximation based on DFT. The structural calculation

reveals that, the CrAs compound is more resistant to volume changes than the MnAs compound. On the other hand, our structural parameters agree very well with the theoretical and experimental data. From the electronic band structure and density of states (DOS) calculations, the CrAs (MnAs) compounds are found to be half-metallic ferromagnets with an indirect gap in the minority spin channel equal to 2.034 eV (1.753 eV) at zero pressure. However, the energy gap mades mainly by hybridization between the *p* states of As and *d* states of Cr or Mn. From the magnetic properties calculation, the results show that the CrAs (MnAs) compounds have an integral magnetic moment 3 $\mu_B$ (4 $\mu_B$) per unit cell, which are following the "$M_t$=$Z_t$ -8" Slater–Pauling rule. The hydrostatic pressure has important effect on the electronic and magnetic properties, resulting in a significant transition from a half-metallic ferromagnetic behavior with 100% spin polarization to metallic behavior for both compounds. The CrAs and MnAs compound have an excellent half-metallic ferromagnetic with high polarization in wide pressure range and represent a good candidate for spintronic applications and other applications.

## ACKNOWLEDGMENT

Technical supports from the (L.E.S.I.M.S) Laboratory, University Ferhat Abbas Setif 1, Setif, Algeria, are gratefully acknowledged.

## REFERENCES

[1] W. E. Pickett and J. S. Moodera, "Half metallic magnets," Phys. Today., vol. 54, pp. 39-45, 2001.

[2] R.A. De Groot, F.M. Mueller, P.G. Van Engen and K.H.J. Buschow, "New class of materials : half-metallic ferromagnets," Phys. Rev. Lett., vol. 50, pp. 2024, 1983.

[3] T. Graf, C. Felser and S. S. P. Parkin, "Simple rules for the understanding of Heusler compounds," Prog. Solid State Chem., vol. 39, pp. 1-50, 2011.

[4] H. Boller, and A. Kallel, "First order crystallographic and magnetic phase transition in CrAs," Solid State Commun., vol. 9, pp. 1699-1706, 1971.

[5] S. Sanvito and N. A. Hill, "Ground state of half-metallic zinc-blende MnAs," Phys. Rev. B., vol. 62, pp. 15553, 2000.

[6] H. Akinaga, T. Manago, M. Shirai, "Material design of half-metallic zinc-blende CrAs and the synthesis by molecular-beam epitaxy, " J. Appl. Phys. Japan., vol. 39, pp. L 1118–L 1120. 2000.

[7] A. Azouaoui, N. Benzakour, A. Hourmatallah and K. Bouslykhane, "Structural, magnetic properties and phase stability of CrAs in the zinc-blende structure : Investigated by first principle calculations and Monte Carlo simulation," Solid State Commun., vol. 323, pp. 114101, 2021.

[8] B. Sanyal, L. Bergqvist, O. Eriksson, "Ferromagnetic materials in the zinc-blende structure," Phys. Rev. B., vol. 68, pp. 054417, 2003.

[9] I. Galanakis, "Surface half-metallicity of CrAs in the zinc-blende structure," Phys. Rev. B., vol. 66, pp. 012406, 2002.

[10] K. Ono, J. Okabayashi, M. Mizuguchi, M. Oshima, A. Fujimori, and H. Akinaga, "Fabrication, magnetic properties, and electronic structures of nanoscale zinc-blende MnAs dots," J. Appl. Phys., vol. 91, pp. 8088-8092, 2002.

[11] T. W. Kim, H. C. Jeon, T. W. Kang, H. S. Lee, J. Y. Lee and S. Jin, "Microstructural and magnetic properties of zinc-blende MnAs films with half metallic characteristics grown on GaAs (100) substrates," Appl. Phys. Lett., vol. 88, pp.021915, 2006.

[12] H. Oomae, S. Trizawa, Y. Jinbo, H. Toyota, T. Kambayashi and N. Uchitomi, "Studies of zinc-blende type MnAs thin films grown on InP (001) substrates by XRD," J. Cryst. Growth., vol. 378, pp. 410-414, 2013.

[13] H. Han, T. Feng, C. Zhang, Z. Feng, M. Li, and K. L. Yao, "The stability and half-metallicity of (001) surface and (001) interface based on zinc blende MnAs," Phys. B : Condens. Matter., vol. 539, pp. 61-65, 2018.

[14] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, J.D. Joannopoulos, "Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients," Rev. Mod. Phys., vol. 64, pp. 1045–1097, 1992.

[15] M.D. Segall, P. J. Lindan, M.A. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark and M.C. Payne, "Firstprinciples simulation: ideas, illustrations and the CASTEP code," J. Phys.: Condens. Matter., vol. 14, pp. 2717, 2002.

[16] J.P. Perdew, K. Burke, M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett., vol.77, pp. 3865–3868, 1996.

[17] D. Vanderbilt, "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism," Phys. Rev. B., vol. 41, pp. 7892–7895. 1990.

[18] I. Galanakis, "Surface half-metallicity of CrAs in the zinc-blende structure," Phys. Rev. B., vol. 66, pp. 012406, 2002.

[19] F. Birch, "The effect of pressure upon the elastic parameters of isotropic solids, according to Murnaghan's theory of finite strain," J. Appl. Phys., vol. 9, pp. 279-288, 1938.

[20] V. H. Etgens, P. C. De Camargo, M. Eddrief, R. Mattana, J. M. George and Y. Garreau, "Structure of ferromagnetic CrAs epilayers grown on GaAs (001)," Phys. Rev. Lett., vol. 92, pp. 167205, 2004.

[21] H. C. Jeon, T. W. Kang, S. U. Yuldashev, T. W. Kim and S. Jin, "Magnetotransport properties of zinc-blende-structured MnAs films with half-metallic characteristics," Appl. Phys. Lett., vol. 89, pp. 112517, 2006.

[22] I. Galanakis and P. Mavropoulos, "Zinc-blende compounds of transition elements with N, P, As, Sb, S, Se, and Te as half-metallic systems," Phys. Rev. B., vol. 67, pp. 104417, 2003.

[23] R. J. Soulen, J. M. Byers, M. S. Osofsky, B. Nadgorny, T. Ambrose, S. F. Cheng, ... and J. M. D. Coey, "Measuring the spin polarization of a metal with a superconducting point contact," science., vol. 282, pp. 85-88, 1998.