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Study of Structural and Electronic Properties of Ternary PdMnGe Half-Heusler Alloy

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***Abstract*—**This study deals with the structural and electronic properties of ternary PdMnGe Half-Heusler alloy using the full potential linearized augmented plane wave (FP-LAPW) method based on the density functional theory (DFT) as implemented in the WIEN2k package, within the framework of generalized gradient approximation (GGA). Structural parameters, total and partial densities of states were also analyzed. The obtained result shows that the studied material is metallic in GGA treatment. The elastic constants (*Cij*) show that our compound is ductile, stiff and anisotropic.

***Keywords*—**Full potential linearized augmented plane wave, generalized gradient approximation treatment, Half-Heusler, structural and electronic properties.

I. Introduction

HEUSLER alloys in general have drawn growing attention during the last few decades in the scientific community [1]. In particular, half Heusler (HH) with generic formula XYZ show a big interest for their properties such as shape memory, thermoelectric, ferromagnetic, spin polarization effects and superconductivity [2]-[10], that could lead to new mechanical and electronic devices. These properties are due to many substitutions of transition elements at both the crystallographic sites X, Y and (III-V) elements at the Z sites.

In the absence of experimental data, a predictive theoretical study of structural, electronic and elastic properties is judged necessary in order to give a global and deep understanding of this ternary HH alloy.

Recently, several studies have been done, proposing an unusual class of HH materials excluding transition metals and rare earth elements, leading to deeper research interest in technology applications. Also HH compounds, such as XMZ (X=Fe, Co and Ni; M=Ti, V, Nb, Zr, Cr, Mo and Mn; Z=Sb and Sn) [11], NiCrZ (Z=Al, Ga, In, P, As, Sb, S, Se and Te) [12]-[14] and hypothetical NiVM (Z=P, As, Sb, S, Se and Te) [15] have been predicted from first principles calculations. In the above mentioned HHs, the magnetic moment is mainly due to the presence of d electrons of transition metals.

This paper is organized as follows. The theoretical background is presented in Section II. Results and discussion are presented in Section III. A summary of the results is given in Section IV.

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II. Computational Method

All HH compound calculations were performed via the FPLAPW method [16]-[20], which is known to be a precise and efficient approach for solving the Kohn–Sham equation within a framework of the DFT as implemented in the WIEN2k code [21], [22]. The GGA proposed by Wu–Cohen (WC-GGA) [23] was used for exchanges and correlation. The separation energy between the core and valence states is kept at − 6.0 Ry.

The integration of the full Brillouin zone is performed with 11 × 11 × 11 k-points mesh, which corresponds to 56 k-points in the irreducible wedge. The self-consistent cycles calculations are considered to be converged when the total energy is stable within 0.1 mRy (10^{-4} Ry).

The wave functions inside the atomic spheres in the full potential scheme for this material are expanded in terms of spherical harmonics up to *l*max = 10. The convergence parameter RMT × *K*max is set to 8. One thousand *k*-points are used for electronic property calculations.

III. Results and Discussion

A. Structural Properties

The HH compounds having the general formula XYZ, where X and Y are transition-metal elements, and Z is a main-group element crystallize in non-centro symmetric cubic MgAgAs (C1b) structure with the F-43m space group. The structure of these compounds arises from three interpenetrating fcc lattices of X, Y, and Z atoms with corresponding Wyckoff positions are 1, 2 and 3 (Table I).

TABLE I
The Sites Occupied by Atoms X, Y and Z for PdMnGe

Types	4a (X)	4b (Y)	4c(Z)
Type1	(0,0,0)	(1/2,1/2,1/2)	(1/4,1/4,1/4)
Type2	(1/2,1/2,1/2)	(1/4,1/4,1/4)	(0,0,0)
Type3	(1/4,1/4,1/4)	(1/2,1/2,1/2)	(0,0,0)

For the case of PdMnGe and in order to determine the equilibrium lattice constants of hypothetical XYZ compounds in HH phase, the total energy as a function of relative volume for three possible atomic arrangements (1, 2 and 3) are evaluated. It is found that this compound is most stable in 1-structure compared to 2 and 3 ones (Fig. 1).

The total energy values as a function of volume are fitted by the empirical Birch-Murnaghan's equation of states (EOS) [24].

The obtained parameters at the static equilibrium are: lattice constant (a_0), bulk modulus (B), its first pressure derivative

(B'), the volume V_0 and minimum total energy (E_0) (Table II).

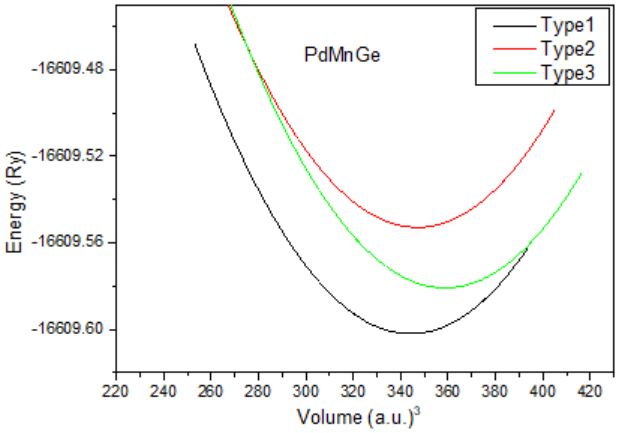

Fig. 1 Total energy as a function of unit cell volume with GGA approximation

TABLE II
EQUILIBRIUM LATTICE CONSTANT A_0(Å), BULK MODULUS B(GPA), ITS PRESSURE DERIVATIVE B', THE VOLUME V_0 AND MINIMUM TOTAL ENERGY (E_0)

Compound	a_0(Å)	B(GPa)	B'	$V_0(u.a)^3$	E_0 (Ry)
PdMnGe	5.88	118.51	4.17	343.03	-16609.63104

B. Electronic Properties

In order to visualize the spin effect on the electronic structure of PdMnGe, we used GGA approach at the equilibrium lattice constant along the high symmetry direction in the first Brillouin zone.

The obtained result shows that this material is metallic due to the overlapping of the valence bands with the conduction ones in which Fermi's level passes through the overlapped regions as shown in (Fig. 2).

For better understanding the electronic properties of the studied HH and to explain the contribution of different states in the band structures, both total density of states using GGA and partial densities of states were evaluated respectively as shown in Fig. 3.

The total density of states (TDOS) graphic shows the existence of three regions:

- The first energy region ranging from -10.45 to – 9 eV is an isolated region of the others, it comes mainly from a significant contribution of the 4s states of the Ge atom.
- The second energy region ranging from -6, to 0 eV is the most important region in the TDOS, which comes mainly from a significant contribution of 4d states of Pd and a small contribution of 3d states of Mn and 4p of Ge atom.
- The third energy region ranging from 0 to 12 eV shifted from the Fermi level is characterized by the strong contribution of the states of the two spins 3d of the Mn atom and the weak contribution of the 4p states of the Ge atom for the two spin states. This p-d hybridization is indicative of the covalent nature of the Mn-Ge bonds.

In addition, the total magnetic moment of PdMnGe is equal to 3.47μB at equilibrium lattice constant. The magnetic moment mainly originates from the strong spin-polarization of 3d electrons of Mn atom (μ_{Mn} = 3.40 μB).

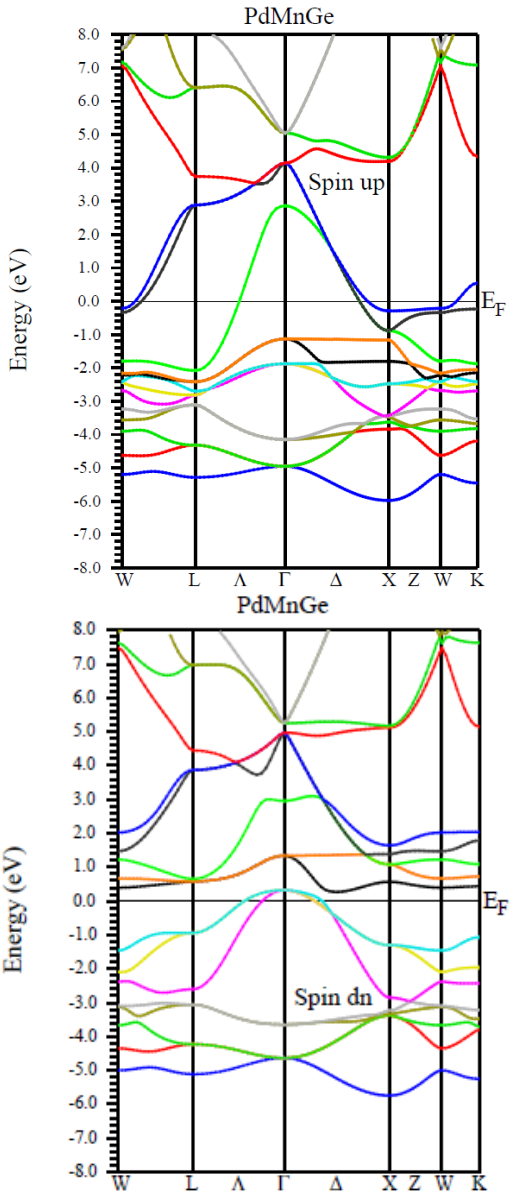

Fig. 2 Spin-polarized band structures of PdMnGe (spin up and spin down)

C. Elastic Constants

Stress-strain method was used to predict the studied compound elastic constants in order to confirm its stability.

We noticed that, there are only three independent elastic constants C_{ij}, namely C_{11}, C_{12} and C_{44} for a cubic system. Their values are summarized in Table III; the above criteria are satisfied meaning that PbMnGe is mechanically stable. We remark that the calculated bulk modulus from the elastic constants such as $B = (1/3)(C_{11} + 2C_{12})$ has nearly the same value as the one obtained from of Birch Murnaghan equation of state EOS fits (see Table I). In addition, other macroscopic parameters such as the anisotropy factor A, shear modulus G, the Poisson's ratio v and the Young's modulus E have also been investigated in this study. These parameters

were calculated using the Voigt-Reuss-Hill approximations for the cubic structures [25]-[27]:

$$B_V = B_R = (C_{11} + 2C_{12})/3 \quad (1)$$

$$G_V = (C_{11} - C_{12} + 3C_{44})/5 \quad (2)$$

$$G_R = 5C_{44}(C_{11} - C_{12})/[4C_{44} + 3(C_{11} - C_{12})] \quad (3)$$

$$A = 2C_{44}/(C_{11} - C_{12}) \quad (4)$$

$$G = (G_v + G_R)/2 \quad (5)$$

Both the Young's modulus E and Poisson's ratio v are given by:

$$E = 9BG/(3B + G) \quad (6)$$

$$v = (3B - 2G)/[2(3B + G)] \quad (7)$$

It is noticed that for a cubic crystal, the necessary mechanical stability conditions should be ($C_{11} - C_{12} > 0$); ($C_{11} + 2C_{12} > 0$; $C_{44} > 0$ and $C_{12} < B < C_{11}$[28].

The obtained results reported in Table III verify clearly these conditions and give credibility to this present study. According to Pugh [29], the bulk-to-shear modulus ratio B/G is an indicator of the materials plastic characteristics. A material is ductile for ratio greater than 1.75; otherwise, it will be fragile and hard. In this study, the B/G ratio for PdMnGe was equal to 2.91 indicating then that the considered material is in fact ductile and, therefore, insensitive to thermal shocks. Poisson's ratio can also be used for estimating the ductility of a material. According to the Frantsevich rule [30], if the Poisson's ratio is $v > 1/3$, the material is considered to be ductile, otherwise, the material is brittle. Based on the results for v values presented in Table III, we can say that our material is ductile in nature. We should also note that the studied compound has an A value greater than the critical one ($A = 1$) of the isotropic material. Thus, we can conclude that this material is anisotropic. Furthermore, we have the Young's modulus (E) (indicating 109.34 GPa), used for providing a measure of the solid stiffness, higher the value of Young's modulus stiffer will be the compound.

TABLE III
CALCULATED ELASTIC CONSTANTS C_{IJ} AND THE BULK MODULUS B (IN GPA), ANISOTROPY FACTOR A, SHEAR MODULUS G (IN GPA), YOUNG'S MODULUS Y (IN GPA) AND THE POISSON'S RATIO Γ OF THE CUBIC PDMNGE

Material	C_{11}	C_{12}	C_{44}	B	A	v
PdMnGe	185.15	85.25	35.35	118.55	0.70	0.36

IV. CONCLUSION

In summary, the structural and electronic properties of PdMnGe compound in HH structure are investigated using GGA approximation within the DFT. The electronic band structure calculation shows that PdMnGe exhibits the metallic behavior with the magnetic moment of 3.47μB at equilibrium lattice constant. The magnetic moment mainly originates from the strong spin-polarization of 3d electrons of Mn atom.

Finally, the obtained elastic constants, such as the shear modulus, Young's modulus, anisotropy factor and Poisson's ratio, demonstrate that the material is ductile, anisotropic and stiff.

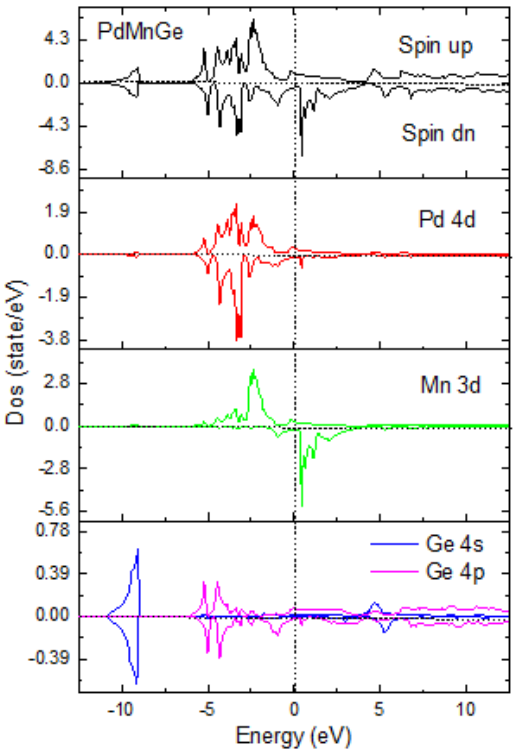

Fig. 3 Total and partial density of states. Fermi level is set to zero

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