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Structural and electronic properties of half-Heusler alloy PdMnBi calculated from first principles

Wenchao Huang [a], Xiaofang Wang [a, *], Xiaoshuang Chen [a, *], Wei Lu [a], L. Damewood [b], C.Y. Fong [b]

[a] National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, China
[b] Department of Physics, University of California, Davis, CA 95616-8677, USA

HIGHLIGHTS

- We studied all different atomic arrangement (α, β, and γ phases) of PdMnBi.
- Detailed explanation of electronic properties for three phases has been given.
- We did observed half-metallic properties in alpha and beta phase.
- The spin-orbital effect is considered and we made a comparison with NiMnSb.

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ABSTRACT

The dependence of the electronic and magnetic properties on the atomic arrangements of three different phases (i.e. α, β, and γ phases), of the half-Heusler alloy PdMnBi, is investigated based on spin-polarized density functional theory. For each phase, the optimized lattice constant is determined and the possibility of finding a half-metal is explored. Throughout this study, the bonding features of each phase are not supported by the large electronegativity of Pd given in the public domain. Both α and β phases PdMnBi show half-metallic (HM) properties for a range of lattice constants, and their magnetic moments are consistent with the values given by the modified Slater-Pauling rule. Additionally, the effects of the spin–orbit (S-O) interaction are examined by comparing the relative shifts of the valence bands and the indirect semiconducting gap, with respect to the spin-polarized results.

1. Introduction

Half-Heusler (HH) alloys have attracted much attention since 1983, when de Groot et al. [1] predicted NiMnSb would exhibit half-metallic properties. Ideally, a half-metal exhibits 100% spin polarization at the Fermi level, E_F, which can lead to applications in spintronics devices, such as spin-FET, spin-LED and spin tunneling devices [2–4]. In addition, for HH alloys, the relatively high Curie temperatures [5–8], and structural similarity to the zinc-blende phase, offer the possibility of integrating magnetic devices into semiconductor technologies. Recently, some of HH alloys were predicted to be topological insulators [9].

In general, an HH alloy, XYZ, has $C1_b$ structure, which is similar to the structure of a full-Heusler alloy (X_2YZ), the $L2_1$ structure, except missing one X. Elements X and Y are transition-metal, while Z is a main group element. The $L2_1$ structure is shown in Fig. 1, and the notations of atom positions are according to Wyckoff [10–13]: $4a=(0,0,0)a_0$, $4b=(1/2,1/2,1/2)a_0$, $4c=(1/4,1/4,1/4)a_0$ and $4d=(3/4,3/4,3/4)a_0$ (a_0 is the lattice constant of the outer cube). Due to the missing X, there are three atomic configurations for XYZ HH alloys, which are called α, β and γ phases [14]. The atomic arrangement of each phase is provided in Table 1.

In this paper, the electronic and magnetic properties of PdMnBi are explored. PdMnBi is a typical HH alloy and has not been studied before. However, it should exhibit interesting bonding properties compared to other transition-metal element based HH alloys, because the electronegativity of Pd on Pauling's scale is 2.20 which is large compared to 1.55 for Mn, 1.90 for Bi, 1.91 for Ni and even 2.05 for Sb [15]. The normal electronic configuration of Pd is $(4d)^{10}(5s)^0$, so it is difficult to construe how the filled *d*-shell will

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* Corresponding authors.
E-mail addresses: wc_huang@mail.sitp.ac.cn (W. Huang), wxiaof66@mail.sitp.ac.cn (X. Wang), xschen@mail.sitp.ac.cn (X. Chen).

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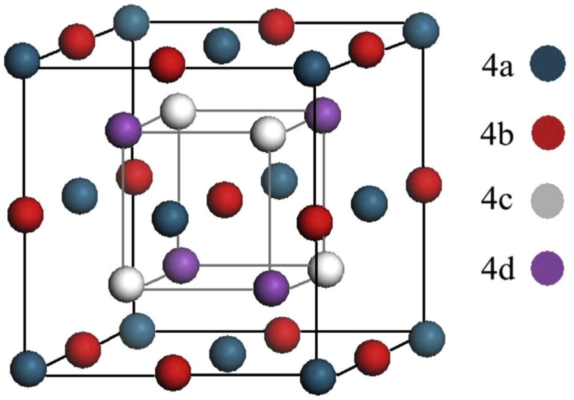

Fig. 1. The $L2_1$ structure (the full-Heusler alloy). Notations of atom positions: 4a = (0,0,0)a_0, 4b = (1/2,1/2,1/2)a_0, 4c = (1/4,1/4,1/4)a_0 and 4d = (3/4,3/4,3/4)a_0, where a_0 is the lattice parameter.

have such large electronegativity. Furthermore, previous results of half-Heusler alloys without Pd [16,17] are consistent with the Pauling's scale of the electronegativities. Brown et al. [18] experimentally and theoretically investigated a similar HH alloys, including PdMnSb, however the large electronegativity of Pd was not addressed. Here is a question: Can the large electronegativity of the Pd manifest in the bonding feature of PdMnBi? In addition, it is well known that the moment per unit-cell for NiMnSb is 4 μ_B [1], where μ_B is the Bohr magneton. Can these three arrangements of PdMnBi have the same moment and can each phase be a half-metal at its respective optimized lattice constant? If a phase is not a half-metal, can it be a half-metal at a lattice constant away from the optimized value? If so, how far will the lattice constant change? Due to the larger sizes of Pd and Bi as compared to Ni and Sb in NiMnSb, should the effect of spin–orbit (S–O) be considered?

In Section 2, a brief description of the computational methodology will be given. In Section 3, structural and electronic properties for each phase of HH PdMnBi at its optimized lattice constant will be presented. In Section 4, the influence of the lattice parameter on the magnetic properties for each phase will be discussed. The question of how far apart from the optimized lattice constant raised in the last paragraph will also be addressed. Also, the effect of S–O interaction will be reported in Section 5. In Section 6, the potential applications of this HH will be discussed. Finally, in Section 7, a summary will be provided.

2. Computational methods

The Vienna ab-initio Simulation Package (VASP) [19] was used to study the electronic and magnetic properties of PdMnBi in the three phases mentioned above. The package uses the pseudopotential approach for characterizing the effects of the ions. The potentials are constructed using the projector augmented wave (PAW) [20–21] method. The generalized-gradient approximation (GGA) was employed to treat the exchange and correlation between electrons [22]. The Monkhorst–Pack scheme [23] with a 15 × 15 × 15 grid was used to calculate the total charge density. Plane-waves are used as basis functions with the kinetic energy cutoff set to 350 eV for all phases. This cutoff energy is sufficient to achieve highly converged results within the PAW scheme. For every alloy, each atom inside the unit-cell is fully relaxed to its equilibrium configuration by calculating the forces on it. In the relaxed configuration, the components of forces are less than 10^{-5} eV Å^{-1}. Calculations for the S–O interaction were carried out using the non-collinear scheme in the VASP algorithm [19].

Table 1
The sites occupied by atoms X, Y, and Z in α, β and γ phases. The 4d site is vacant.

	4a	4b	4c
α phase	Z	Y	X
β phase	X	Y	Z
γ phase	Z	X	Y

3. Structural and electronic properties in optimized situation

Fig. 2 shows the total energy vs. the lattice constants of α, β and γ phases of PdMnBi. The optimized lattice constants are 6.39, 6.47 and 6.32 Å for α, β and γ phases, respectively. The optimized lattice constants, total energies, and calculated magnetic moments are summarized in Table 2. The most energetically favorable atomic arrangement is the α phase, while the γ phase has the smallest lattice constant. These results are attributed to the facts: (i) In the α phase, Pd forms the nearest neighbor (nn) pairs with both Bi and Mn, while Bi has both Mn and Pd as nn pairs for the β phase. (ii) The size of Pd is larger than the one for Mn. Thus, a strong bond is formed between Bi and Pd leading to the lowest total energy in the α phase. In the γ phase, Bi is not in nn configuration with the Pd.

The charge distributions in the same section of the three phases are shown in Fig. 3. The triangular and elongated contours around the Bi atom in the α and β phases show there are bond formations close to the Bi atom. This suggests that charge transfers from the other two atoms to Bi. In the γ phase, the Mn atom has both Pd and Bi as nn pairs, and Pd and Bi are second neighbors. The larger electronegativity of Bi can pull Mn in, which gives the smallest optimized lattice constant. The bond between Bi and Mn is stronger than the bond in the β phase. All these results do not indicate any effect of large electronegativity of the Pd.

The total magnetic moment *M*, in units of μ_B per unit-cell for each phase is given in Table 2. For the β phase, the value 4.023 μ_B/unit-cell is closest to an integer. As will be shown later, the modified Slater-Pauling rule for HH alloys determines that half-metallic PdMnBi should have a moment of 4 μ_B/unit-cell.

The magnetic properties of half-metals in zinc blende (ZB) structure can be attributed to three competing mechanisms: (1) Crystal field effect spits the *d*-states of Mn (in this case it can even be the Pd) into a triply (t_{2g}) and a doubly (e_g) states. (2) The triplet states interact with the sp^3-type of states of the Bi to form bonding and antibonding states. (3) The exchange interaction changes the populations of the spin up and down states. The remaining electrons at the Mn site form the local moment of the crystal. Since the HH alloys have structure close to the ZB structure, the moments given in Table 2 can be attributed to the electrons remaining at the Mn site.

The values of *M* in the three phases can be qualitatively explained based on the configurations of the neighbors as follows: In the α phase, due to the second neighbor configuration of Mn and Bi, the fact that small charge transfer from Mn to Bi, leaves most of the *d*-electrons at the Mn and gives the largest magnetic moment. For the β phase, Bi is nn to both Pd and Mn. Electrons at the Mn are transferred to the Bi to form *d*–*p* bonds. Thus, it leaves fewer electrons at the Mn site than in the α phase to form the moment. The Mn atom in the γ phase is neighboring both Pd and Bi. Due to the fact that Mn has the smallest electronegativity, Mn loses most of its electrons. In all the cases, the *d*-electrons remaining at the Mn align their spins under the first Hund's rule to form the local moment.

Fig. 4 illustrates the three spin-polarized band structures of PdMnBi determined at the respective optimized lattice constant of the phases. The left side is for the majority spin channel and the