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A comparative study of different exchange-correlation functionals in understanding structural, electronic and thermoelectric properties of Fe_2VAl and Fe_2TiSn compounds

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ABSTRACT

Fe_2VAl and Fe_2TiSn are full Heusler compounds with non-magnetic ground state. The two compounds are good thermoelectric materials. PBE and LDA (PW92) are the two most commonly used density functionals to study the Heusler compounds. Along with these two well studied exchange-correlation functionals, recently developed PBEsol, mBJ and SCAN functionals are employed to study the two compounds. Using the five functionals equilibrium lattice parameter and bulk modulus are calculated. Obtained values are compared with experimental reports wherever available. Electronic structure properties are studied by calculating dispersion curves, total and partial density of states. For Fe_2VAl, band gap of 0.22 eV is obtained from the mBJ potential which is in reasonable agreement with experimental value while, for Fe_2TiSn band gap of 0.68 eV is obtained. Fe_2VAl is predicted to be semimetallic with different values of negative gaps from LDA, PBEsol, PBE and SCAN functionals. Whereas, Fe_2TiSn is found to be semimetallic (semiconducting) from LDA, PBEsol (PBE,SCAN) functionals employed calculations. From the dispersion curve effective mass values are also computed to see the contribution to the Seebeck coefficient. In Fe_2TiSn, a flat band is present along the Γ-X direction with calculated value of effective mass ~36 more than the mass of electron. The improvements or inadequacies among the functionals in explaining the properties of full Heusler alloys for thermoelectric application are thus observed through this study.

1. Introduction

Electronic band structure of a material tells about the occupation of electrons at different energy levels in that material. The electronic structure is studied through experimental methods like photoemission spectroscopy as well as through theoretical tools such as DFT, DMFT methods. Electrical conductivity, thermal conductivity, Seebeck coefficient are the transport properties of a material which is decided by electronic structure of that material. So, transport properties can be well explained by understanding the electronic structure of the material. For a thermoelectric material, it's efficiency is determined by figure-of-merit (ZT) and it is governed by these transport properties [1,2]. To improve and modify a material as an efficient thermoelectric of practical application, a good understanding of it's electronic structure is essential. So, the methods of electronic structure analysis should be accurate enough to model the material with physical accuracy.

First-principles density functional theory (DFT) [3] method is the most resorted methods for the theoretical evaluation of electronic structure of periodic solids today. In the Kohn-Sham (KS) [4] form of DFT, the KS equation is solved self-consistently for the one electron wave functions. In the KS equation the electron-electron interaction part is approximated by the exchange-correlation potential. The limitation of DFT in exactly modelling electronic structure is introduced from this part. So, there is a large research in the development of electron exchange-correlation functionals for better approximations. Thus, many density functionals exist today with it's own merits and demerits. The limitations of DFT functionals is that they may be quite accurate for some physical properties, while it may not be accurate for other physical properties of the same material [5]. Some functionals are constructed for explaining specific applications.

Local density approximation of Perdew and Wang-1992 (LDA-PW92) [6] and generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [7] are the two most widely used functionals in the first-principles DFT calculations. In the LDA, local exchange-correlation potential is defined as the exchange potential for the spatially uniform electron gas with the same density as the

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local electron density [5]. LDA is less suitable for prediction of the properties of atoms and molecules, since the density is not slowly varying in case of atoms and molecules. In GGA functionals, electron density is described using both the local electron density and gradient of electron density. PBE is an improved description of the local spin density approximation for atoms and molecules [7]. GGA calculations are found to improve upon LDA for atomization of energies of molecules and enthalpy of formation derived from the atomization energy [8]. But, for nonmolecular solids, the lattice parameters calculated by PBE are not found to improve. Also, it is known that LDA underestimates lattice constant, while PBE overestimates. PBEsol functional was proposed by a restoration of the density-gradient expansion in PBE [9]. This functional is intended to provide accurate values of equilibrium properties for solids and their surfaces. Also, PBEsol is supposed to give better values of lattice constant in the densely packed solids and in solids under pressure. mBJ potential was proposed by Tran and Blaha, by modifying the exchange potential originally put forth by Becke and Johnson. This semilocal potential is claimed to yield accurate band gaps for semiconductors and insulators and is less expensive than the hybrid and GW calculations [10]. SCAN is a semilocal meta-GGA approximation which is fully constrained [11]. This functional is expected to be a significant improvement over PBE, PBEsol and LDA functionals, at the nearly same computational cost.

The research on Heusler family of compounds is drawing more attention due to it's interesting applications. The application of Heusler alloys include in spintronics and energy harvesting. Many groups are studying the Heusler compounds for spintronics applications, for eg. Co based Heusler alloys and it's thin films are studied towards applicability in spintronics [12–14]. Some half-Heusler alloys are also proposed as topological insulators [15]. Full Heusler alloys are good candidates as thermoelectric materials for heat energy utilisation. For instance, S. Sharma et al. have studied the full Heusler alloys in the view of thermoelectric applications [18,17]. Number of studies on full Heusler alloys using LDA, PBE or mBJ functionals are available in literatures. But, a comparative study on full Heusler alloys, with different exchange-correlation functionals which influences in deciding the thermoelectric behavior is missing. Fe_2VAl and Fe_2TiSn are compounds belonging to class of full Heusler alloys with formula unit of the form X_2YZ, where X and Y are transition metal elements and Z is a main group element [19]. The two compounds have non-magnetic ground state with zero magnetic moment as given by Slater-Pauling rule for full Heusler alloys [20]. The two compounds are good thermoelectric materials. Their properties are studied experimentally as well as using first-principles calculations. Experimentally, Nishino et al. reported that Fe_2VAl-based full Heusler alloys are showing large power factor (PF = $S^2\sigma$, where S is Seebeck coefficient and σ is electrical conductivity) considerably more than that of the conventional thermoelectric material Bi_2Ti_3 [21]. In first-principles DFT based study of full Heusler compounds, LDA of Perdew Wang (1992), PBE are more commonly used functionals to investigate the thermoelectric properties. Markus Meinert investigated the properties of full and half Heusler alloys using modified Becke-Johnson potential [19]. Sharma et al. used PBEsol exchange-correlation functional to study thermoelectric properties of the full Heusler alloys and showed the possibility of synthesis in laboratory [18].

In the present work, taking up Fe_2VAl and Fe_2TiSn as representatives of non-magnetic class of full Heusler alloys we are interested to check the suitability of these exchange-correlation functionals for the calculation of the properties of full Heusler alloys with non-magnetic ground states. The properties approximated from the new functionals are compared with the well used functionals (LDA, PBE) used to study this kind of compounds. We have employed five exchange-correlation functionals to study: (i) structural properties of the two Heusler compounds. Lattice constant and bulk modulus values are extracted from energy versus volume curves and the obtained values are compared with the available experimental data. (ii) Dispersion curves, total and partial density of states are calculated to study the electronic structure. General features and differences in the electronic structure predicted from different functionals are discussed. For the two compounds effective mass values are computed from the dispersion curve using parabolic approximation. The values of effective mass are used to give an idea of contribution to Seebeck coefficient.

2. Computational details

The calculations are performed using the full-potential linearized augmented plane wave (FPLAPW) method as implemented in the WIEN2k [22] program for calculating crystal properties within density functional theory. For the exchange-correlation part five different functionals are used viz., LDA of Perdew-Wang-1992 (LDA) [6], GGA of Perdew-Burke-Ernzerhof (PBE) [7], and newly developed PBEsol [9], mBJ [10], and SCAN [11]. In case of mBJ, for the correlation part LDA is used with the modified Becke-Johnson (mBJ) potential for the exchange part. The muffin-tin radii R_{MT} used for volume optimization calculations of (i) Fe_2VAl are 2.26 bohr for Fe; 2.15 bohr for V and 2.04 bohr for Al (ii) Fe_2TiSn are 2.32 bohr for Fe;2.26 bohr for Ti; 2.32 bohr for Sn, respectively. A k-mesh grid of size $10 \times 10 \times 10$ is used for both volume optimization and electronic structure calculations. The self-consistency in the total energy/cell is achieved by setting a convergence criteria of 0.1 mRy.

The equilibrium lattice constants are computed by fitting the total energy versus volume of the unit cell data to the Birch-Murnaghan (BM) equation of state [23]. The third-order BM isothermal equation of state is given by the formula:

$$E(V) = E_0 + \frac{9V_0B_0}{16}\left[\left\{\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right\}^3 B_0' + \left\{\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right\}^2 \left\{6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right\}\right] \quad (1)$$

where E is energy, V is volume, B_0 is equilibrium bulk modulus, V_0 is volume of experimental unit cell and B_0' is pressure derivative of bulk modulus at equilibrium value. The volume optimization process is carried out by varying the lattice parameters in a fixed ratio.

Fe_2VAl and Fe_2TiSn have the space group $Fm-3m$ and they are found to crystallise in cubic $L2_1$ structure. Denoting these two full Heusler compounds as Fe_2YZ, where Y = V,Ti and Z = Al,Sn in the order, Fe atoms occupy the Wycoff position 8c $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, Y atoms occupy Wyckoff position 4a $(0,0,0)$ and Z atoms occupy Wyckoff position 4b $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. We employed 5 different exchange-correlation functionals to study these compounds. The results are discussed in the sections below.

3. Results and discussion

3.1. Structural properties evaluation

In order to find the theoretical lattice constants of Fe_2VAl and Fe_2TiSn, calculations are carried out for several values of volumes corresponding to different lattice constants employing the five exchange-correlation potentials mentioned in Section 2. The obtained values of total energy is plotted as a function of volume. The Birch-Murnaghan (BM) parameters are used to fit the calculated data. The fitted curve gives the equilibrium lattice constant and bulk modulus value. 5.762 Å[24] and 6.074 Å[25] are the reported values of experimental lattice constants for Fe_2VAl and Fe_2TiSn, respectively. These experimental values of lattice