

Influence of the Exchange-Correlation Functional on the Energy of Formation and Magnetic Behavior of Binary $D0_3$ Intermetallic Compounds FeM_3 ($M = Ti, Zr, Hf$)

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Abstract In recent years, ab-initio calculations based on the density functional theory became a commonly used tool in supporting, improving or even refuting experimental results in different research fields. In this work we discuss some accuracy aspects inherent to ab-initio electronic structure calculations regarding the understanding of different structural, electronic and magnetic physical properties. In particular, we discuss the dependence of the magnetic ground-state and the formation energy with the exchange-correlation functional for the binary intermetallic compounds $FeTi_3$, $FeZr_3$ and $FeHf_3$ with $D0_3$ crystal

structure. All exchange-correlation schemes used were based on the generalized gradient approximation. It is the aim of the present paper to call the attention of the community to some fundamental aspects of the calculations that can influence the final results and the conclusions derives from it.

Keywords ab-initio calculations · formation energy · magnetism

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1 Introduction

Ab-initio (or first-principles) calculations in the framework of the Kohn–Sham scheme of the density functional theory (DFT, Ref 1,2) has been established nowadays as one of the most popular methods of choice to predict structural, electronic, magnetic and other properties of solids. In principle, DFT is an exact method. A DFT prediction for a given magnitude or property should be identical to the experimental determination of this property at zero Kelvin (within usual error bars), provided a perfect (single or poly) crystal is used in the experiment and zero-point motion effects are negligible. In practice, however, one has to make an assumption in the DFT calculations for the unknown exchange-correlation functional. This assumption limits the agreement between prediction and experiment, leading to deviations between theory and experiment (“intrinsic errors” in Ref 3) and introduces an error bar on the predicted physical magnitudes.

The treatment of exchange and correlation effects has a long history and is still an active field of research (see, for example, Ref 4–6). In the initial times of DFT, results from quantum Monte Carlo calculations^[7] for the homogeneous electron gas (for which the problem of exchange and correlation can be solved exactly) were used leading to the

original local density approximation (LDA, Ref 8). Surprisingly LDA works reasonably well but has some shortcomings mostly due to its tendency to overestimate binding energies and, in consequence, prediction of equilibrium volume of crystals that are smaller (by a few percent) than the experimental ones. Maybe the most “famous” error of LDA is the incorrect prediction for the ground state of metallic Fe.

The next step in DFT was the implementation of the generalized gradient approximation (GGA), for example the version by Perdew, Burke and Ernzerhof (PBE)^[9] which improved LDA by adding a term corresponding to the gradient of the electron density. Contrary to the tendency of LDA, the PBE approximation always predicts larger lattice constants. For several cases this approximation gives better results than LDA and thus for a long time PBE has been the standard for many solid state calculations. In recent years, however, several improvements of GGA were proposed.^[10, 11] Besides these improvements of the theory, there are properties (cohesive energy, magnetic properties, band gaps, etc.) that depend on the functional and not all functionals work equally well for all properties and all systems. In other words, one functional can predict a result that is very different from those obtained using other functionals (the mentioned case of the equilibrium structure of metallic Fe, for example). Since there is no recipe the methodological warning is: perform calculations using different exchange and correlation functionals and compare the predictions. It is important to realize that such procedure only gives a “measurement” of the difference among the different exchange and correlation functionals and no guarantee that the prediction using the unknown “real” functional would be within this error margin.¹ In fact, DFT calculations using LDA or different parameterizations of GGA disagree even qualitatively with experimental data and can lead, for instance, to the prediction of a metal instead of an insulator.

In recent years, ab-initio calculations have gained an important role in supporting, improving, or even refuting experimental results in new research fields. This “expansion” of the ab-initio calculations was mostly due to the fact that it became popular and available to everyone in user-friendly computer packages. One of these fields is the

thermodynamics of alloys and compounds,^[12, 13] being recognized as a powerful tool that can provide standardized, reliable and eventually complementary information to experimental data. In particular, ab-initio calculations were used in combination with the CALPHAD method (CALculation of PHase Diagrams^[14]). This method is a fast and efficient way to describe equilibrium phase diagrams of systems such as alloys, molten salt mixtures and steelmaking slags. In order to take full advantage of the method, values must be assigned to parameters related to formation energies of compounds, which may be difficult to measure experimentally. In these cases, the ab-initio calculations can provide reliable and accurate information that cannot be obtained experimentally.

In the present work, we discuss the dependence of the magnetic ground-state and formation energies with the exchange and correlation functional for a set of highly symmetric binary superlattices of the BCC structure. These compounds, namely, the $\text{DO}_3\text{-FeM}_3$ ($M = \text{Ti, Zr, Hf}$), present cubic symmetry and no internal positional degrees of freedom such that simple and extremely well converged calculations can be performed. All calculations have been performed using the Full Potential-Linearized Augmented Plane Wave Method (FP-LAPW, Ref 15–17) considering different exchange and correlation schemes based on the GGA: PBE,^[9] PBEsol^[10] and WC.^[11] It is the aim of the present paper to call the attention of the community to some fundamental aspects of the DFT calculations, which are known to the experienced researcher, but not so much to the broad newcomers in the field. We will use simple FeM_3 DO_3 compounds as prototype systems to perform illustrative tests on how structural, electronic, magnetic and formation energies can be affected by the choice of computational details and the exchange and correlation scheme. We will show here that careful studies have to be performed before we arrive at conclusive results and how the results depend on the choice of the exchange and correlation potential.

2 Calculation Details

For all FeM_3 compounds ($M: \text{Ti, Zr, Hf}$), we have considered the cubic crystal structure DO_3 , with space group $Fm\text{-}3m$ (225), see Fig. 1, where the Fe atom is located in the $4a$ Wyckoff position (0,0,0), and the M atoms are located in the $4b$ and $8c$ Wyckoff positions: (1/2, 1/2, 1/2) and (1/4, 1/4, 1/4), respectively.

The spin-polarized electronic-structure calculations based on the DFT have been performed with the Wien2k implementation^[18] of the FP-LAPW method^[15–17] in a scalar relativistic version without spin-orbit coupling. The exchange and correlation effects were treated using

¹ In order to determine the intrinsic error (for a given system) a comparison with accurate experimental results or with high-level quantum chemistry methods must be done. Only a comparison with accurate experimental results or with high-level quantum chemistry methods must be done. Quantum Chemistry methods are highly accurate, can reach an almost exact solution and do not suffer from the choice of an exchange-correlation functional, but the computational effort dramatically increases with the number of atoms and in practice they can only be obtained for relatively small systems (atoms or small molecules). When the system size is larger (as in condensed matter) these methods are unavoidable.

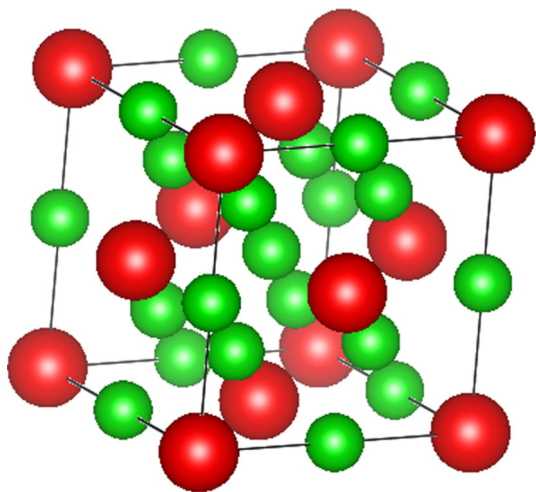


Fig. 1 D₀₃ FeM₃ unit (cubic) cell: Fe (red) and M (green)

different parameterizations of the GGA, namely PBE,^[9] PBEsol^[10] and WC.^[11] These last two functionals have been shown to be especially good for 3d and 4d transition metals.^[19]

In the FP-LAPW method the wave functions are expanded in spherical harmonics inside non-overlapping atomic spheres of radius R_{MT} (muffin-tin radii) and in plane-waves in the remaining space of the unit cell (the interstitial region). The value of R_{MT} used for Fe and the M elements was 1.05 Å. Once a choice is made for the exchange and correlation functional in DFT, the Kohn–Sham equations are fully determined. A DFT code solves those equations numerically and in principle this leads to solutions/predictions that are numerically exact. In this procedure additional errors will be introduced (“numerical errors”). The most important parameters for keeping the numerical errors small are the basis set size and the density of the mesh used for Brillouin zone sampling. An advantage of plane-wave based methods is that the convergence of their basis set can be tested easily by including additional plane waves in the calculations. This was done for several cases here and extremely well-converged solutions were found when the parameter $R_{MT}K_{MAX}$ (which controls the size of the basis set in these calculations) was equal to 9 (R_{MT} is the smallest atomic radius and $R_{MT}K_{MAX}$ the largest wave number of the basis set). Integration in the reciprocal space was performed using the tetrahedron method taking 20000 k -points in the first Brillouin zone. For the calculations of the density of states (DOS), a denser k -mesh (200000 k -points) was considered. In order to check the accuracy of the present results we performed several additional calculations. We studied the convergence in the basis set by varying the $R_{MT}K_{MAX}$ value from 7 to 10. We also increased the number of k -points from 20000 to 50000 and we also studied the effect of the R_{MT}

on the relevant properties of the systems under study. Magnetic moments and energy differences can be obtained with convergence errors smaller than $1 \times 10^{-2} \mu_B$ and 1×10^{-3} eV using $R_{MT}K_{MAX} = 9.0$ and 20000 k -points. So, we can conclude that the numerical errors are negligible. Finally, we restrain our analysis to collinear ferromagnetism.

3 Results

For the three systems under study, FeZr₃, FeTi₃ and FeHf₃, the total energies were calculated self-consistently considering different values for the cubic lattice parameter (a). The Birch-Murnaghan equation of state (EOS)^[20] was fitted to the obtained energy versus a data, $E(a)$ to determine the equilibrium lattice parameters of each compound (other structural properties, i.e., the bulk modulus B and its derivative with respect to pressure, can be easily determined using this approach, see Ref 20). In Fig. 2 we present the $E(a)$ curves corresponding to the three systems under study and for all the exchange and correlation functionals considered here. The obtained equilibrium lattice parameters (a_0) for each system are presented in Table 1. As can be seen, WC and PBEsol predict nearly the same lattice parameters (differences smaller than 0.2%). PBE predicts lattice parameters that are 2% larger than those predicted by PBEsol and WC. This difference is small and, in a “minimum-effort approach”, one could then be tempted to conclude that this difference would not lead to any serious discrepancies and all the exchange and correlation schemes will conduce to identical results for electronic and magnetic properties. This assertion could be true in some cases, but, as we will see, these 2% difference in the lattice parameters can lead to very different results for other quantities, and studies for different exchange and correlation parameterizations must be performed prior to formulate any conclusion.

If we put the attention on the magnetic properties of FeM₃ compounds, an important difference is observed in the description of the magnetic state of these systems. Using PBE, a net total magnetic moment (μ_T) is obtained for all compounds studied here. When WC or PBEsol functional are employed, the equilibrium state is characterized by $\mu_T = 0.00 \mu_B$ (see Table 1). In Fig. 3, we show the variation of μ_T with a for all the compounds and the different approaches for the exchange and correlation functional. The dotted lines in Fig. 3 represent the value of the predicted a_0 for each exchange and correlation used (reported in Table 1). It can be seen that for small values of a , μ_T is zero in all cases; when a increases, μ_T also increase in a nearly parabolic behavior. This behavior is similar for all the exchange and correlation approaches considered, the

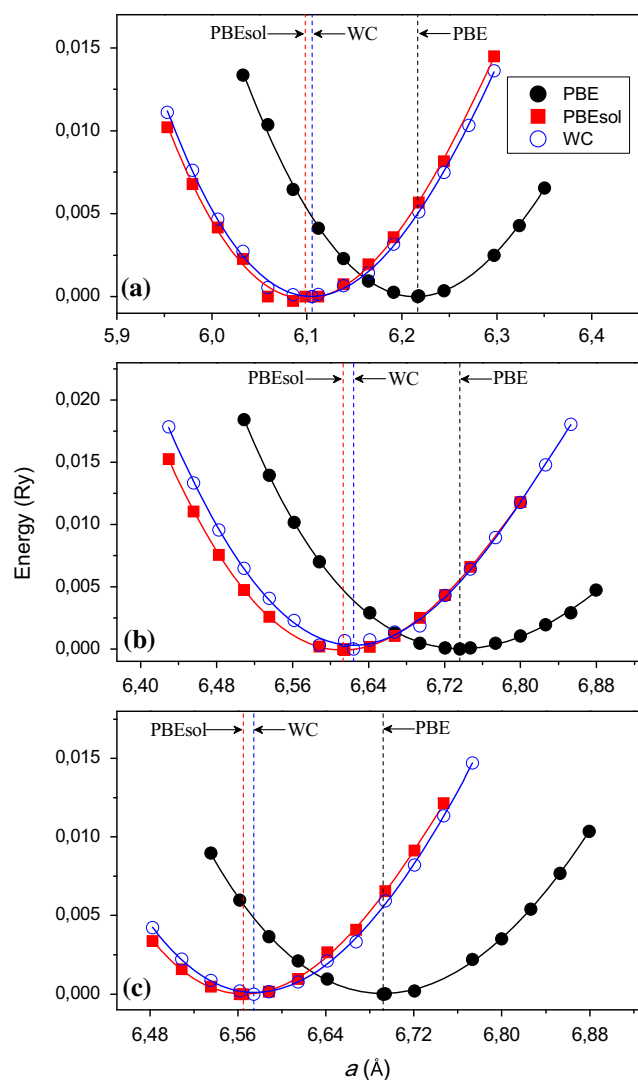


Fig. 2 Total energy as a function of the lattice parameter curves for (a) FeTi₃, (b) FeZr₃ and (c) FeHf₃ compounds using different parameterizations of the GGA functional

Table 1 Predicted equilibrium lattice parameters (a_0) and total magnetic moment per unit formula for the different exchange and correlation functional employed here

	a , Å			μ_T , $\mu_B/u.f.$		
	PBE	PBEsol	WC	PBE	PBEsol	WC
FeTi ₃	6.217	6.099	6.106	2.36	0.00	0.00
FeZr ₃	6.736	6.613	6.624	1.00	0.00	0.00
FeHf ₃	6.692	6.565	6.575	1.00	0.00	0.00

Numerical errors due to the basis set and the density of the mesh used for Brillouin zone sampling are smaller than 1×10^{-3} Å and $0.01 \mu_B/u.f.$

difference is the threshold μ_T value for which a net magnetic moment is predicted. It is important to note that FeTi₃ is an interesting case because the predicted value for a in

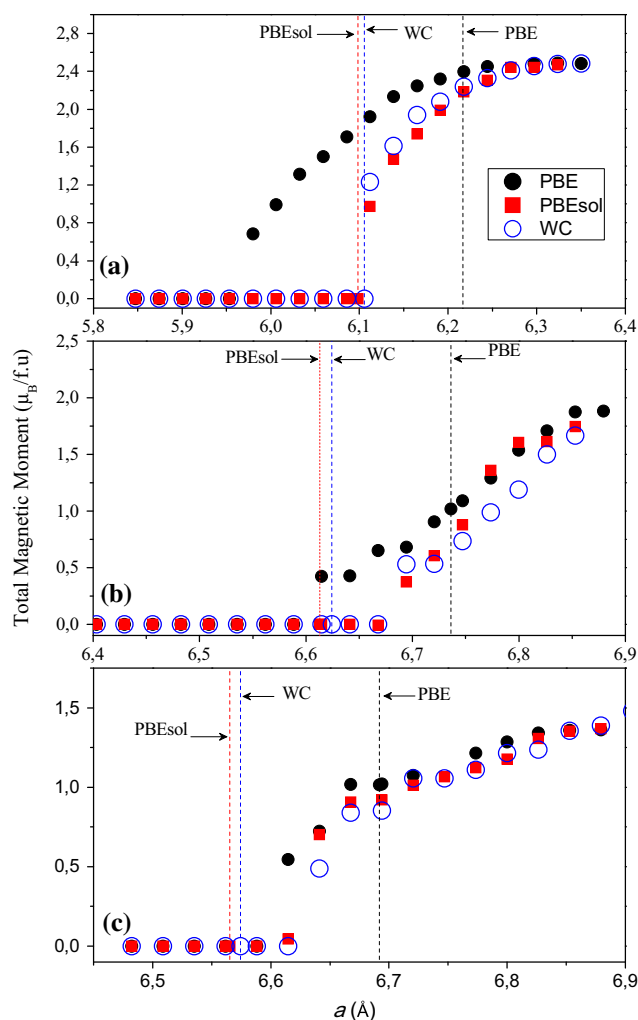


Fig. 3 Variation of total magnetization μ_T with cubic lattice parameter a for (a) FeTi₃, (b) FeZr₃ and (c) FeHf₃ using the PBE, PBEsol and WC functionals

the PBEsol and WC calculations is in the limit where μ_T begins to take values greater than zero, showing that small variations in the determination of a could lead to a different magnetic state. It is clear in this case the “sensitivity” of ab-initio calculations for the determination of structural and magnetic ground states, and how much care must be taken to determine it. Clearly, a detailed convergence study (basis set, number of k-points) must be done to determine the numerical error in order to obtain physically valid results.

We can conclude that calculations using PBE leads to a very different result to those obtained with PBEsol or WC, even when a similar lattice parameter is predicted for all the exchange and correlation functionals.

In order to further determine the magnetic stability of the systems under study we performed calculations of the energy difference $\Delta E(\mu_T) = E(\mu_T) - E(\mu_T = 0)$ as a function of μ_T . For this study, fixed spin moment

calculations were performed varying μ_T in the range 0.00–3.50 μ_B /u.f. In Fig. 4 we present the obtained results for $\Delta E(\mu_T)$. Since the results obtained in the WC and PBEsol calculations are very similar (differences are included in the size of the points) for the sake of simplicity and for a better comparison we will present the results obtained using PBE and WC only. As can be seen, in all cases PBE predict a ground state characterized by $\mu_T > 0.00 \mu_B$ /u.f. (minimum of the curve $\Delta E(\mu_T)$). The energy barriers between the magnetic ground states and the $\mu_T = 0$ magnetic states are 3.95, 0.45 y 0.63 meV for FeTi₃, FeZr₃, and FeHf₃, respectively. When the WC scheme is used, the favourable states are the $\mu_T = 0$

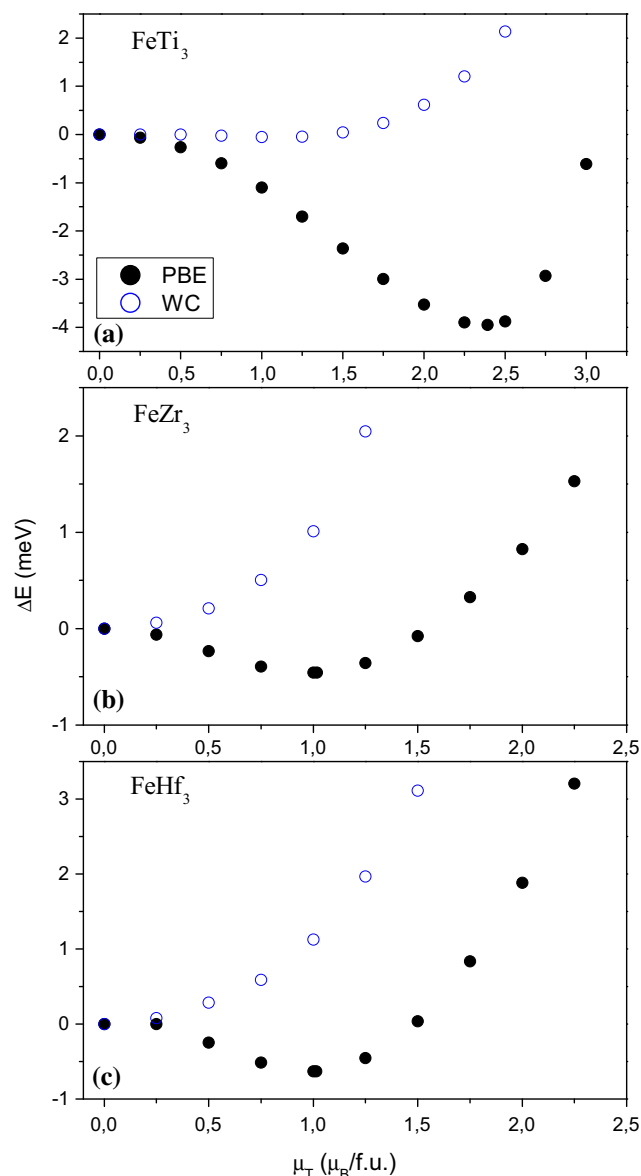


Fig. 4 Dependence of ΔE with μ_T for (a) FeTi₃, (b) FeZr₃, and (c) FeHf₃ for the PBE and WC calculations

magnetic ones and the energy barriers increase exponentially with μ_T (see Fig. 4).

The difference between PBE and WC (or PBEsol) calculations can be clearly observed in the density of states (DOS) of the FeM₃ compounds. In Fig. 5 we present the DOS and the atom-resolved (partial DOS, p-DOS) for the case of FeZr₃ obtained in the WC and PBE calculations. The different magnetic character obtained using PBE or WC/PBEsol is related to the different population of the up and down states of the Fe atom (3d-Fe).

The last point studied was the formation energy of the studied FeM₃ compounds ($^f U_{Fe_p M_q}$). This energy is defined as:

$$^f U_{Fe_p M_q} = \frac{{}^0 U_{Fe_p M_q} - p {}^0 U_{Fe} - q {}^0 U_M}{p + q} \tag{Eq 1}$$

where ${}^0 U_{Fe_p M_q}$ is the total energy of the FeM₃ compound, ${}^0 U_{Fe}$ and ${}^0 U_M$ are the total energies of the Fe and M atoms, and p and q are the number of Fe and M atoms in the compound $Fe_p M_q$ i.e., the stoichiometry of the compound (in the present work, $p = 1$ and $q = 3$). ${}^0 U_{Fe}$ and ${}^0 U_M$ were obtained from metallic BCC-Fe ($a = 2.8665 \text{ \AA}$, Ref 20)

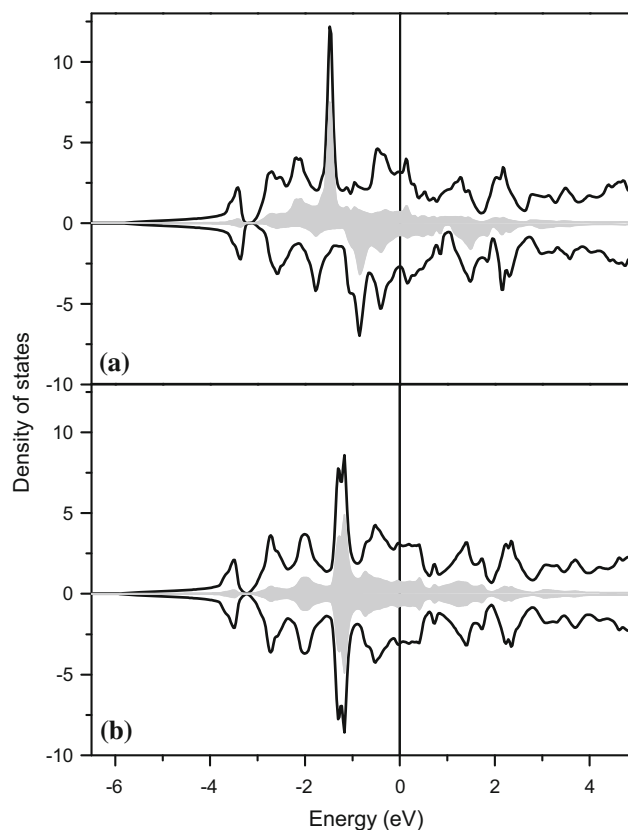


Fig. 5 Total (black lines) DOS and Fe-partial Density of states (gray area) for DO₃ FeZr₃. The results correspond to calculations performed with (a) PBE and (b) WC functionals. Energies are referred to the Fermi Level

Table 2 Formation energy (kJ/mol of atoms) for the three FeM₃ compounds studied in this work using PBE and WC functionals

	FeTi ₃	FeZr ₃	FeHf ₃
PBE	−20.4	65.7	80.4
WC	−41	44.8	57.8

and HCP Ti, Hf, and Zr and ($a = 2.9508 \text{ \AA}$, $c = 4.6855 \text{ \AA}$ for Ti; $a = 3.2320 \text{ \AA}$, $c = 5.1470 \text{ \AA}$ for Zr; $a = 3.1964 \text{ \AA}$, $c = 5.0511 \text{ \AA}$ for Hf, Ref 21–24), respectively, with the same precision as that in the FeM₃ calculations.

In Table 2, we present our results for the formation energies for the three compounds under study in the calculations performed using the PBE and WC schemes. As can be seen, in the three cases the formation energies obtained using WC are nearly 21.0 kJ/mol of atoms smaller than those obtained using PBE. This is a not negligible difference: in the case of TiFe₃, PBE predicts a formation energy twice as large than those predicted by the WC calculation. In conclusion, the magnitude of such commonly quantity, used largely in the calculation of phase diagrams and thermodynamic properties, is very sensitive to the exchange and correlation functional, and a careful study must be done prior to draw any conclusion.

4 Conclusion

We have performed an ab-initio DFT study of structural, magnetic and formation energies using a well-established all-electron method (LAPW). We have used three simple intermetallic compounds (FeM₃, M = Ti, Zr, Hf) with the DO₃ structure as prototype systems to perform illustrative tests on how the mentioned properties can be affected by the choice of the exchange and correlation scheme and computational details. Performing convergence tests is a well-known basic task to be achieved before arriving at a conclusive prediction of a given observable. We also show here that it is very important to always perform a careful study of the exchange and correlation scheme to be adopted. Only after these careful tests are made the comparison of experimental data with results obtained using, as in this work, “state of the art” ab-initio methods, can be properly done, and meaningful physical information will be obtained.

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