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Comparative study between LMTO and FPLAPW into the calculation of the electronic structure of carbide $Cr_{23}C_6$

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Abstract

Considering the actual state of the art in Materials Science, it is necessary to do a theoretical analysis of the compounds obtained through experimenting, with the objective of understanding them better, by foreseeing their behaviour and possible new compounds. For this, in this work, we calculate electronic structures of $Cr_{23}C_6$ chromium carbide, which are present in fast steels, using two methods of calculating the band structure of first principles, the method of linear muffin-tin orbital (LMTO) with the Andersen's atomic sphere approximation (ASA) and the method of linear plain and expanded waves (LAPW) with generalized gradient approximation (GGA). Through calculations of formation energy in relation to its volume we obtain the equilibrium volume of 379.16 u.a. using the LMTO, and 375.13 u.a, using the LAPW. In the equilibrium volume we calculated some fundamental state properties. We observed an extremely low magnetization in both methods; nevertheless, in LAPW we verified a little magnetic moment in the CrI site that is $0.2512\mu_B$. The method LAPW affirms the existence of an interstitial region motivating the charge transference to this region. As the LMTO does not have the interstitial region, we do not see the charge transference to this region; in this case the charges come out of the C and CrI sites to take place in the CrII site. The density of states (DOS) shows that there is an interaction between the "s" states of C with the other sites and in a more intense way with the CrII site. When we compared the DOS, in relation to the methods used, we saw that in case of the LMTO, these are slightly placed in regions where energy is lower as well as its Fermi energy.

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1. Introduction

New experimental techniques put forward some elements that need to be studied from the theoretical point of view. Two very much used examples of experimental techniques are the plasma nitration [1,2] and mechanical alloying [3,4]. For an accurate theoretical analysis of a compound, we need to use a comparison among some calculation methods, inside the theoretical models of electronic structure, being the answer of the present work. Like this, having a more accurate vision of the properties of the ground-state of new compounds that are being experimentally studied is now possible.

Based on the fact that it is theoretically possible to study stages separately, we chose to work with chromium carbides that present crystalline cubic lattice. We modelled an FCC type unit cell with five atoms in the base to represent the $Cr_{23}C_6$ chromium carbide with a chromium atom at the corner (CrI), three chromium atoms in the face (CrII) and the interstitial C.

Our work is focused on elucidating some queries about charge transference, magnetic moment and bulk modulus of chromium carbides, present in a great variety of linked steels, as in cold and hot work steels. It is suggested that, during plasma nitration, chromium carbides can be transformed into chromium nitrides [5] showing the importance of theoretically understanding these compounds. We verify, therefore, the importance of developing theoretical methods for the study of properties of

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compounds, so as to allow the extrapolation of theoretical results for the understanding of experimental processes. This way, the improvement of materials properties will be possible, as well as the projection of new materials.

In properties calculation of the ground-state of $Cr_{23}C_6$ we used two models of calculation. We used the density functional theory (DFT) and the local spin density approximation (LSDA). In the second model we included the effects in the place of spin density using the generalized gradient approximation (GGA).

In the first case, linear muffin-tin orbital calculations were performed, within the atomic sphere approximation (LMTO-ASA) [6,7] to study the magnetic and electronic structures of the $Cr_{23}C_6$ compound. For these calculations we took the crystal structures of these compounds as simple cubic, where the CrI atoms occupy the corner sites and the CrII atoms, the face-centred positions while the carbon atoms occupy the body-centred sites. We performed spin-polarized LMTO calculations using the Vosko–Wilk–Nusair parameterization for the exchange-correlation energy of the electron gas [8]. Our LMTO calculations were made without spin–orbit interaction but including the combined correction terms [6]. For the fully ordered Cr_4C compounds the Wigner–Seitz spheres (Si) around CrI and CrII atoms were taken to be of equal size. The Wigner–Seitz values were obtained using $(\frac{4}{3})\pi \sum Si^3 = a^3$ (where a is the lattice parameter). For the carbon we take $SC = 0.5SCr$. The one-electron potentials were self-consistently obtained using reciprocal space sums with 455 k-points. The self-consistent cycles were carried out until energy convergence on a scale better than 0.5 mRy was achieved. The solutions of the Schrödinger equations use "s", "p" and "d" LMTO basis functions. The densities of states (DOS) were calculated as a sum of delta functions for a fixed number of lattice points and the energy window was divided into a lattice of 1500 points.

In the second approach the linear plain and expanded waves (LAPW) method [9] was employed. The calculations are based on the DFT with the GGA to the exchange-correlation potential [10]. The muffin-tin radius was taken as 1.70 Å for all the atoms. Inside the muffin-tin spheres the charge densities, the potentials and wave functions are expanded in terms of the spherical harmonics and the cut-off angular momentum (l_{max}) is 10 for the wave functions and 6 for the charge densities and potentials. To ensure convergence for the Brillouin zone integration 1000 k-points were used in the whole Brillouin zone, employing the improved tetrahedron method [11]. The number of augmented plane waves included was about 80 per atom, that is $R_{mt}K_{max} = 8$. To calculate the DOS 750 k-points were used in the whole Brillouin zone. Self-consistency was achieved by demanding that an inter-band charge transfer is smaller than 10^{-6} electrons, which corresponds to a convergence of the total energy better than 0.1 mRyd.

In this article we initially discuss equilibrium volume, bulk modulus, and after that we approach the electronic structure itself by evaluating some of the properties of ground-state, as well as the influence of pressure in the states, density. Last but not least, we present conclusions remarking the importance of the methods being used.

2. Result and discussion

The calculations of total energy Fig. 1 of formation versus volume, were done for some lattice parameters, with a variation of 2% in each calculation, being so we obtained 379.16 u.a theoretical equilibrium volume during the LMTO method. This implicates in a 7.2378 u.a. equilibrium lattice parameter. With the LAPW, the calculated equilibrium volume was 375.13 u.a., what implicates in a 7.220 u.a lattice parameter. Comparing both results, using LMTO and LAPW, we observe that there are little differences, being important to remark that in case of LMTO we needed to use an approximation due to the fact of having an overlap between the spheres that are in CrII face and the one of C that is in the centre of the cell, what results in a slightly less accurate calculation of total energy in the LMTO.

For bulk modulus we obtained 281 GPa using LMTO and 266 GPa using LAPW. The difference between the obtained values can be explained when using a LSDA for the calculation with LMTO [7] and a GGA with non-local effects for the LAPW [9,10]. As well, the superposition between the atomics spheres of CrII and C for the LMTO method causes a superposition of wave function influencing the results of the system's total energy of formation [13]. We observe that the values of bulk modulus are in the same order of greatness of substituted iron nitrides [13] but with smaller values than γ-Fe_4N. As an example of substituted iron nitrides we can cite $PdFe_3N$ with a 444 GPa bulk modulus, $SnFe_3N$ with 367 GPa and $MnFe_3N$ with 266 GPa, all these values obtained using the LMTO model. Using the LAPW model we have $AlFe_3$ with 181 GPa, $AlFe_3N$ with 223 GPa and

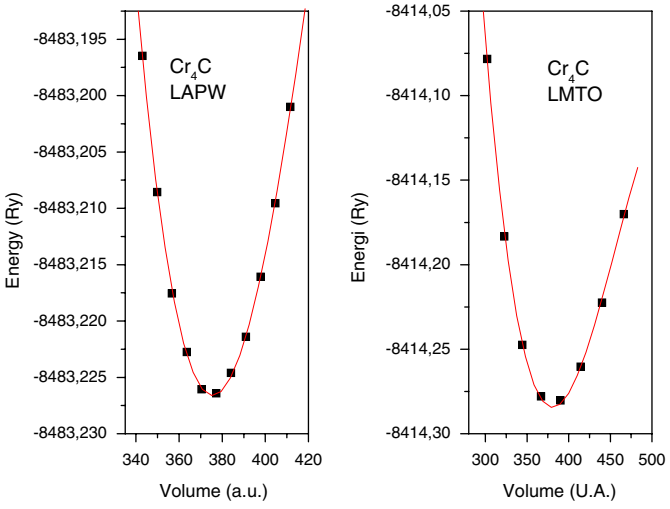

Fig. 1. The calculations of total energy of formation (Ry) versus volume (a.u.).