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Pressure Influence on the Stability and Formation of $\gamma - Fe_4N$ when Transformed into Fe_4O

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The improved technology has allowed the study of electronic structure of solids with a complex crystalline structure and containing various atoms, different in the unit cell, and thus we can calculate the energy of formation and obtaining the bulk modulus and cohesive energy, which lets us discussing the compounds stability. The importance of this work is to obtain the ground state properties of solids face the crystal lattice deformation when subjected to pressure. The nitrogen replacement by oxygen in the interstitial structure $\gamma - Fe_4N$ forming Fe_4O was studied. Calculations indicate that the critical pressure to transform the ferromagnetic into non-magnetic phase is greater in the $\gamma - Fe_4N$ 528,8851 Kbar showing a greater magnetic character. Regarding the resistance to uniform compression (bulk modulus), our calculations show that $\gamma - Fe_4N$ is higher, because a bulk modulus of 281.4045 GPa for non-magnetic phase and 173.7893 GPa for Fe_4O 251.3927 GPa for non-magnetic and 170.1810 GPa for ferromagnetic, showing that the non-magnetic phase have higher bulk modulus for both compounds.

Keywords: *perovskite, nitrides, electronic structure, energy of formation, cohesive energy, LAPW, stability, oxides*

1. Introduction and Literature Review

In the late 20th century calculations began to be treated under a new view, thus conceiving more accurate results in shorter time. Therefore, combining materials engineering, theoretical physics and modern computational techniques, we are able to calculate the ground state properties of solids containing various atoms in the unit cell. Currently, results can be found by experiments[1,2] and others uniting theoretical and experimental physics[3]; however these are very expensive and require advanced laboratories. The computational methods[4-6] provides the calculation of the energy of formation, of cohesion energy and obtains the bulk modulus[7-9]. The results presented here are based on density functional theory[4]. It is used in physics and chemistry to study the electronic structure and ground state properties of many body systems, in particular of atoms, molecules in the condensed phase. Therefore, with the help of computers and the software WIEN2K[10] is possible to study the properties of solids.

Among a wide range of compounds used by man, one of the most important is the class of oxides, which are binary chemical compounds formed by oxygen atoms with other elements. Oxides constitute a large group in the chemistry because most of the chemical elements form oxides. Only this abundance would justify a study on the oxides. However, we will be more specific in our work, since here we studied the Fe_4O oxide, because these materials have a well-defined structure, the perovskite. Some recent experimental papers written by brazilian authors[11] explain about the structure of perovskite oxides, but leave poor research using quantum models that give us information about the properties of the ground state of oxides. In this article, the electronic structure is solved, obtained the ground state properties of the Fe_4O, oxide and its comparison with some results obtained from $\gamma - Fe_4N$, which also has the same perovskite structure.

To modeling our calculations we used a unit cell model with FCC structure (face-centered cubic). With the Iron I atoms in the corner site, Iron II is housed on the site of faces. In the octahedral site there is the nitride in the nitrogen and the oxygen in the oxide as shown in Figure 1. About nitride, a particular reference of 1992 made a study on both theoretical and experimental data thereby opening the area for several subsequent studies[3]. Another study that deserves emphasis for its abundance of results is the one peformed by Eitel L. et al.[12], which uses many calculation models to find the properties of $\gamma - Fe_4N$. But all calculations performed $\gamma - Fe_4N$ still leave some gaps as the energy of formation and cohesion energy, which provides the real balance volume, ie when the pressure is zero. When we found the minimum of cohesion energy allowing us to obtain more precisely the properties of the ground state, we find that the oxide and the nitride still needs the explanation of some properties under pressure. The above is the reason for performing this work, as well as the prospect of helping to further understand the compounds, which will allow in the near future modeling new and better alloys. The article will be presented as follows: first, the computational method used and the details pertaining to the computational part and the state equation are presented. After, results are discussed and finally, there are the final remarks.

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2. Computational Method and Equation of State

2.1. *Computational method*

Our calculations are based on density functional theory with generalized gradient approximation (GGA) and exchange-correlation potential. The method used is the LAPW (Linear Augmented Plane Waves), which is an APW modification (Augmented Plane Wave Method of Slater), inserted of Wien2k computational code[10]. The basic idea that led us to the LAPW base construction is based on the fact that the crystalline potential is approximately plane in regions distant from the nucleus. Therefore, the solution of the Schrödinger equation[6,12] can be expressed as a linear combination of a reasonable number of plane waves. Moreover, the potential undergoes great oscillations near the nucleus, because the solution requires combining a large number of plane waves.

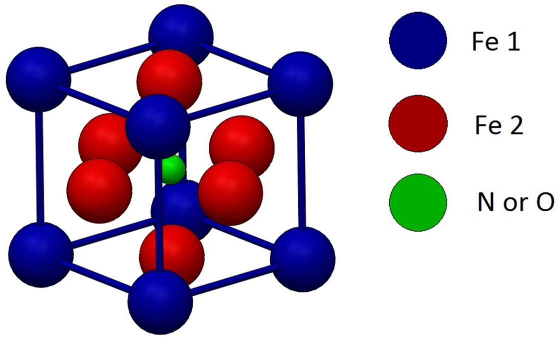

Figure 1. Cell unit model.

Therefore, the electronic wave functions are best represented by the product of two factors: one is the radial function, equivalent to the solution of the Schrödinger radial equation[6,10] with spherical part of the crystalline potential and the other describing the angles dependence through spherical harmonics[6,10]. As a result, crystalline space is divided into two distinct regions, namely the region within the sites and the interstitial region in which the different sets of base are used. The total energy of the LAPW method is given when we solve the Hamiltonian (1):

$$H = -\sum_{i}^{N}\left(\frac{h^2\nabla_i^2}{2m} + \frac{Ze^2}{\vec{r}_i - \vec{R}}\right) + \sum_{i}^{N}\frac{q^2}{\vec{r}_i - \vec{r}_j} \qquad (1)$$

The terms of the equation in order: electrons kinetic energy, coulombic potential energy - nucleus-electron and electron-electron.

2.2. *Equation of state*

The equation of state describes the study of matter in a certain set of physical conditions. It is a constructive equation providing a mathematical link between two or more variables associated with the matter such as temperature,

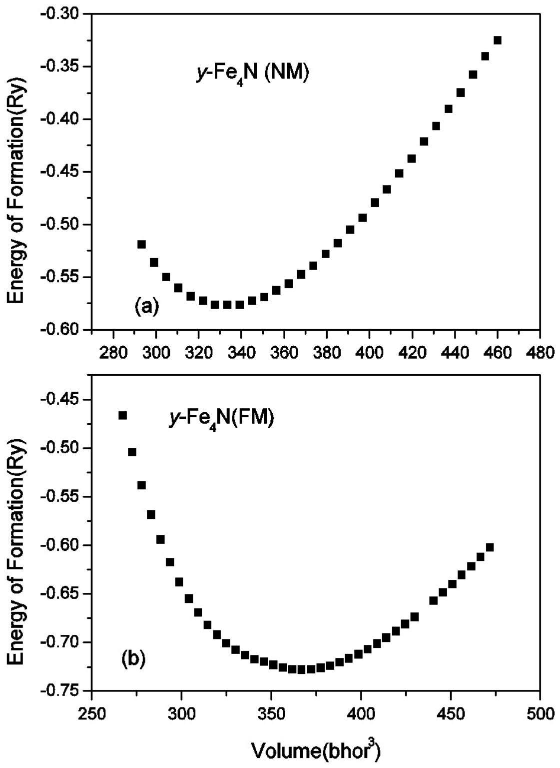

Figure 2. Energy of formation depending on the volume of nitride $\gamma - Fe_4N$ in ferromagnetic and non-magnetic phases.

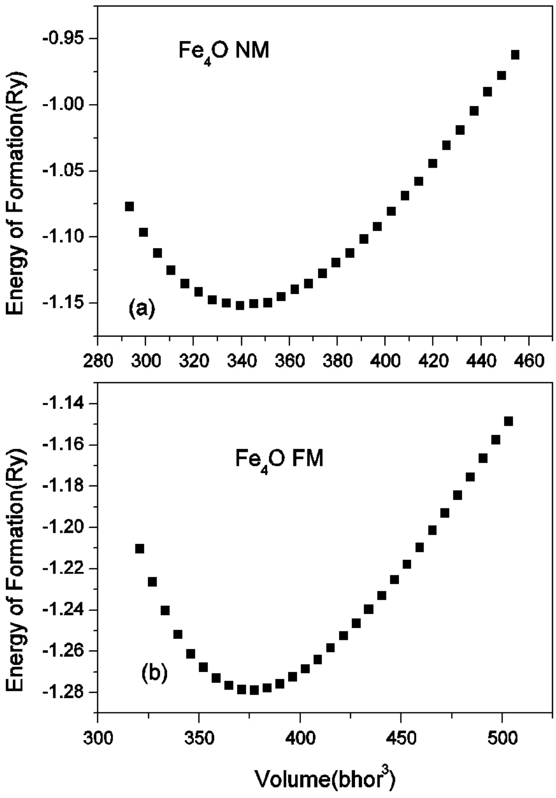

Figure 3. Energy of formation depending on the volume of oxide Fe_4O in ferromagnetic and non-magnetic phases.

pressure, volume or its internal energy. Isometric properties are obtained, such as bulk modulus: $B=-V_0\frac{dP}{dV}$, where $\frac{dP}{dV}$ is the first derivative of pressure with respect to volume. Thus, $B=-V_0\frac{dE^3}{dV^3}$, where $\frac{dE^2}{dV^2}$ is the second derivative of the energy depending on the volume. There is B'_0 which is the first derivative of the bulk modulus in relation to pressure, as $B'_0=-V_0\frac{dB_0}{dP}$. Thus, $B=-V_0\frac{dE^3}{dV^3}$, i.e. using the equation of state we can obtain the total energy of the system studied depending on the pressure.

Currently we can find many uses for the new package for calculating lattice constants and equation of state for hexagonal and tetragonal structure[13], where was performed a convenient volume and a structure optimization by using 2D-Optimize package. The cell parameters and the bulk modulus of twenty hexagonal structure compounds were calculated using the new package and compared with the experimental data.

As a result, the bulk modulus, energy of formation and cohesive energy are obtained. In the next section we will discuss and define the equation for the energy of formation and cohesive energy in order to discuss the compounds stability.

3. Discussion of Results

3.1. *Stability of oxide and nitride*

Calculations were performed in the ferromagnetic phase, where two spin directions were used. In calculating the non-magnetic phase was chosen only one spin direction. Initially we calculated the total energy in function of unit cell volume of iron, oxygen and nitrogen in its bulk form. Thus, the energy of formation (or enthalpy of formation) is obtained, which is given by $E_F = E_{tot} - \sum E_x^i$; where E_x^i is the total energy of each constituent atom of the compound in equilibrium, in its bulk structure. In turn, E_{tot} is the compound's total energy[14-16]. Overall, the energy that is consumed to form the oxide or nitride. Table 1 shows the energy of formation in Rydberg for compounds in the ferromagnetic phase (FM) and non-magnetic phase (NM). The compound that most requires energy for its formation is the Fe_4O in its non-magnetic phase and needs to be supplied -1.2786 Ry per unit cell. We also found that the energy of formation is linked proportionally to the crystalline lattice spacing, since the highest energy of formation has the highest lattice parameter, 3.8125 Å from the oxide in the non-magnetic phase (NM). In Figures 2 and 3 there is the plot for energy of formation depending on the volume for the nitride and oxide in both ferromagnetic and non-magnetic phases. The lowest energy of formation has the lowest lattice parameter, 3.6552 Å from the nitride $\gamma - Fe_4N$ during the non-magnetic phase. Therefore, it can be concluded that it is more favorable energetically to form the nitride $\gamma - Fe_4N$ than the oxide Fe_4O.

To discuss stability, we are required to calculate the cohesive energy, which is defined as the energy required to separating the atoms composing a solid[16]. The cohesive energy varies with the distance between the atoms of a solid (unit cell volume) and reaches a minimum. The cohesive energy value corresponding to such minimum is termed equilibrium cohesive energy, ie the point where the pressure is zero. Therefore, the cohesive energy can be calculated by using the following equation: $E_{coh} = E_{tot} - \sum_n^x E_{ix}^{atom}$ where E_{tot} is the compound's total energy, E_{ix}^{atom} is the energy of each atom constituent of the compound in its free state. Here the cohesive energy per unit cell I used, different from the articles[17-19] that used by atom. Table 1 shows that the $\gamma - Fe_4N$ is the most stable at the ferromagnetic phase, since it is necessary to provide -2.2723 Ry for taking the equilibrium; which was expected since the compound has been found experimentally with a experimental lattice parameter of 3.7950 Å recently measured[18]. This occurs if we compare with other methods seen on reference 12, where they use the total energy of the compound to find the equilibrium lattice parameter. So, using the cohesive energy, we get better results, showing that the theory agrees with the practice.

In Table 1 we find the usual critical pressure which a ferromagnetic material undergoes a transition to a NM phase defined as $P_c = -\Delta E/\Delta V$ where E is the difference between non-magnetic and ferromagnetic equilibrium energies (per atom) and ΔV is the difference between non-magnetic and ferromagnetic equilibrium volumes. We can find that the highr pressure should be performed in $\gamma - Fe_4N$ 528,8851Kbar to pass it from the ferromagnetic to the non-magnetic phase.

In Figures 4 and 5 there is the plot for cohesive energy depending on the volume for the nitride and oxide in both ferromagnetic and non-magnetic phases. Fe_4O is the less stable among compounds, which requires only -2.0465 Ry to separate its crystalline structure into free atoms. The most sensitive cohesive energy to the lattice spacing is the Fe_4O, once a slight change in volume causes a great change in energy.

The bulk modulus calculation, which represents the change in volume when subject to total energy variation, represented by the equation: $B = -V_0 dE^2/(d^2V)$ where

Table 1. Parameters calculated Energy of formation in (Ry), Balance volume in (bhor^3), Cohesive energy (Ry), Lattice parameter (bohr).

Composto	Energy of Formation(Ry)	Cohesive Energy(Ry)	Lattice Parameter(A°)	Bulk modulus(GPa)	Critical Pressure(Kbar)
γ-Fe_4N NM	–0,5762	–2,1762	3,6552	281,4045	
γ-Fe_4N FM	–0,7294	–2,2723	3,7950	173,7893	528,8851
Fe_4O NM	–1,1515	–2,0465	3,6901	251,3927	
Fe_4O FM	–1,2786	–2,1735	3,8125	170,1810	489,7059

$dE^2/(d^2V)$ is the second derivative of the energy with respect to the volume because V_0 is the minimum volume of the compound's total energy. The graphs containing the compound's total energy are not shown in this study by not being imperative. Table 1 shows the Bulk modules in ferromagnetic and non-magnetic phases; the largest Bulk modulus is the $\gamma - Fe_4N$ NM. The non-magnetic phase always has a bulk modulus larger than the ferromagnetic one, once the electron spins are at the same direction, we must provide more energy to cause changes in the system, since the bulk modulus depends on the electron cloud of atoms.

The transformation from a ferromagnetic into a non-magnetic phase may be performed by submitting a ferromagnetic compound to a pressure, which we call the critical pressure. There is some works related to the pressure magnetization decrease in the structure of iron compounds[20-23]. Thus, the pressure required to transform a ferromagnetic state into a non-magnetic will be calculated. Calculations show that the highest pressure is related to the nitride 52.8851 GPa Here we can announce the greater ferromagnetic character of nitride compared to the oxide.

To finish this section, the cohesive energy of compounds will be addressed depending on pressure. We begin by describing in Figures 6a, b the cohesion energy as a function of pressure. Typically, the state equations (EOS) proposed by Murnaghan[16-18] are used to find the balance lattice parameter through the compound's total energy. In this work the cohesive energy was used by being more correct from the theoretical point of view and also by providing better results. Here, we confirm the results obtained for the balance lattice parameter, since the cohesive energy of the equilibrium point, i.e. pressure equal to zero, is the same where volume of equilibrium was found. For this purpose, it is just comparing Figures 6a, b with Figures 3a, b. As a result, we note that the minimum point in the curve of cohesive energy depending on the cell volume is the same where the pressure is zero, i.e. the equilibrium volume, confirming our calculation model through cohesive energy.

4. Final Remarks

Initially, the energy of formation (or enthalpy of formation) was obtained. We note that the compound which requires more energy for its formation is Fe_4O in the non-magnetic phase, i.e. the compound most difficult to form. The energy of formation is related to the crystalline lattice spacing, as the highest energy of formation has the highest lattice parameter and the lowest energy of formation has the lowest lattice parameter. We can thus conclude that energetically, it is more favorable to form the nitride $\gamma - Fe_4N$, than the oxide Fe_4O.

We found that the most stable is the $\gamma - Fe_4N$ in the ferromagnetic phase, which was expected since the compound is more easily found experimentally. Comparing with other methods viewed in reference 12, where the compound's total energy is used to find the equilibrium lattice parameter, using the cohesive energy we got better

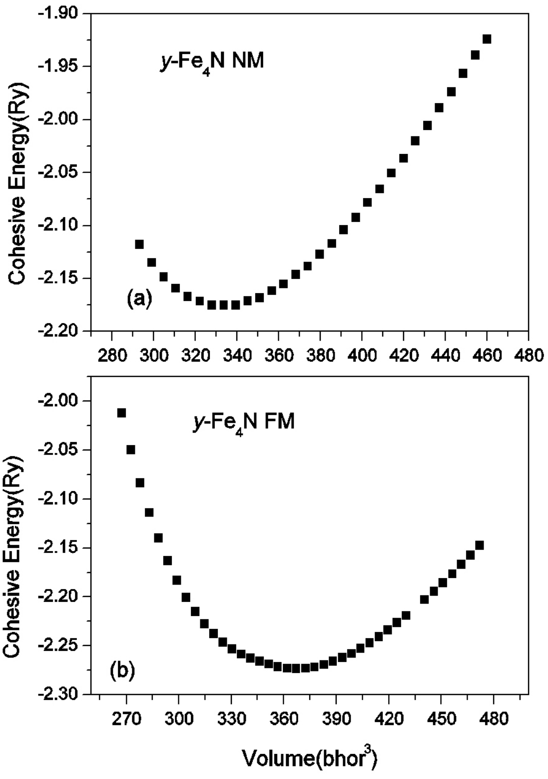

Figure 4. Cohesive energy depending on the volume of nitride $\gamma - Fe_4N$ in ferromagnetic and non-magnetic phases.

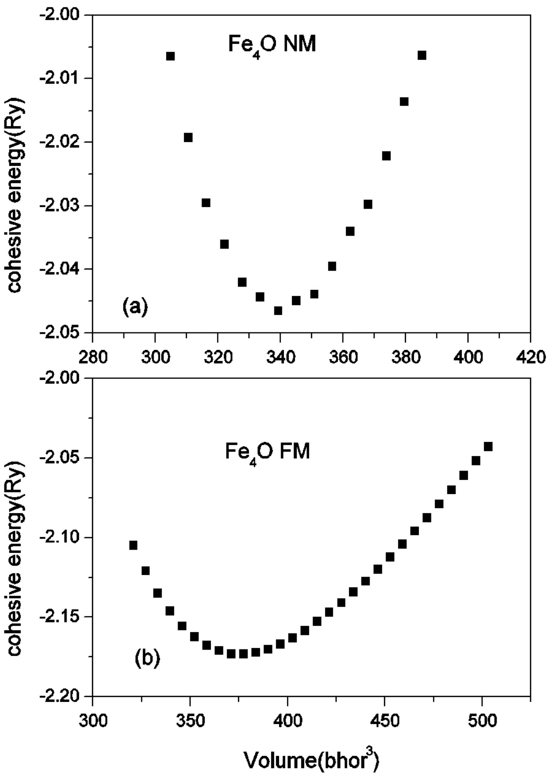

Figure 5. Cohesive energy depending on the volume of oxide Fe_4O in ferromagnetic and non-magnetic phases.

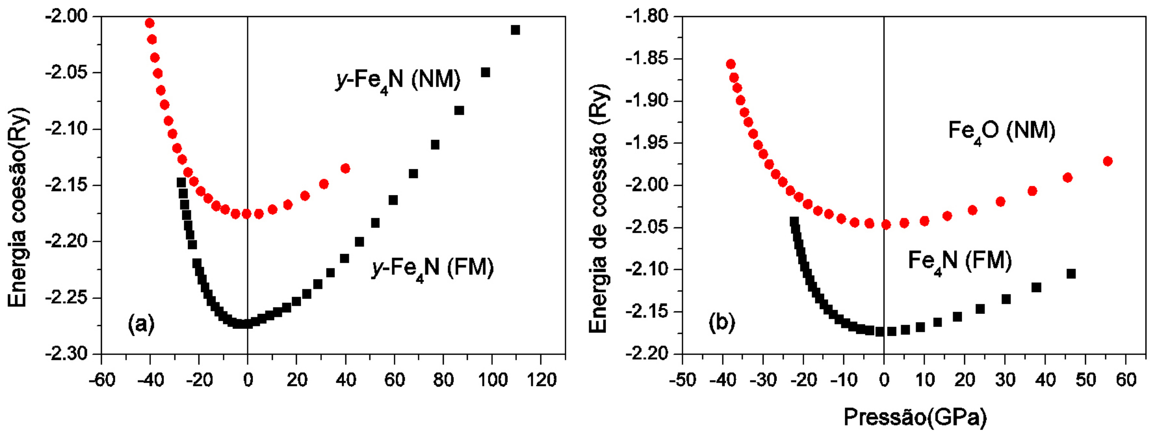

Figure 6. Cohesive energy depending on the pressure of nitrite $\gamma - Fe_4N$ and oxide Fe_4O in ferromagnetic and non-magnetic phases.

results showing that the theory agrees with the practice. The largest bulk modulus is $\gamma - Fe_4N$ NM, in which we found that the non-magnetic phase has always a bulk modulus greater than the ferromagnetic, because as the electron spins are in the same direction, we need to provide more energy to cause changes in the system. Regarding pressure, the highest is related to nitride. We can then infer that the greater ferromagnetic character is that of nitride compared to oxide.

Finally, when confirming the results for the balance lattice parameter, since the cohesive energy of the equilibrium point, i.e. pressure equal to zero, is the same where volume equilibrium is found. Thus, we can say that theoretical works like this can be used in order to guide proposals for experimental works and always performing a test of the methodology used in the calculations.

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