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SOMETHING ABOUT THE PROPERTIES OF FEGE AND FESE

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Abstract

Place holder Initial stages of the epitaxial manganese nitride growth on the (111)-(2×2) indium nitride surface were studied by first-principles calculation within the density functional theory formalism including spin polarisation. The computational calculations were performed using the PWscf program of the quantum espresso suite, where the electro-ion interactions were treated according to a pseudopotential approach and the exchange-correlation energy is modelled using the generalised gradient approximation. First we studied the adsorption of Mn atoms on high symmetry places, varying the coverage from $\frac{1}{4}$ to a full monolayer. The results showed the T4 site as the most optimal geometry. Then, Mn incorporation was investigated, this occurs when an Mn atom displaces an In atom from the first layer, with the In become the new adatoms to be adsorbed. The results yielded – as the most favourable structure. Electronic properties were determined by performing density of states (DOS) and projected density of states (PDOS) calculations for the most favourable structures (repeated). For all the different test, the DOS is non zero at the Fermi level, indicating they all are metallic.

Keywords: Density functional theory, Epitaxial growth, Indium nitride, Manganese Nitride.

1 Introduction

In recent years new studies about the structural, electronic, and magnetic properties of transition metal composites have emerged because of their possible applications in the field of spintronics. In this area, it is important to determine the efficient alignment of the electronic spin. One important type of system are the diluted magnetic semiconductors (DMS) that incorporate of transition metals. DMS monolayers with polarized spins allow an injection of polarized electrons into metal-semiconductor interfaces, that is why it is important to know the spin alignment in heterostructures and interfaces. Gallium (Ga), manganese (Mn) and Arsenic (As) (Ga1-xMnxAs) have been investigated because they possess magnetic properties, however, they also have a low Curie temperature.

2 Density Functional Theory

Modelling atomic, molecular or solid systems is a complex and difficult task. There are just a few systems that have complete analytical solutions. It is true that we could obtain useful information using workarounds and approximations, such as perturbation theory, for more difficult, yet small systems. Nevertheless, for most problems of interest, and their corresponding applications, models are constructed with dozen or hundreds of atoms, and here a computational method is required.

It is known that most properties of a given system can be obtained using just total energies and differences in total energies. For example, for the case of a solid, from total energy calculations (and it's subsequent minimisation with respect to the nuclear coordinates) properties like lattice constant, bulk moduli, phonos, pizoelectric constant, phase-transitions pressures and temperatures could be obtained. There exist plethora of energy calculations theories and algorithms. Nevertheless, the density functional theory (DFT) was chosen for performing all calculations, as it is optimised for periodic systems. In the following sections, the basic of the theory, requirements and approximations used will be explained.

This theory's first approach to convert this problem in a more manageable one is to use the Born-Openheimer approximation. It states that because the nuclei are many times more massive than the electrons, the electrons respond instantaneously to any modifications on the coordinates of the nuclei. This statement allows us to separate electronic and nuclear coordinates. To solve and electronic problem for a given frozen arrangement of the ions.

For that reason, it is convenient to divide the overall method in four parts, as follows:

1. Electron electron interactions: treated within the DFT theory

2. Periodic and aperiodic systems: usage of a plane waves basis sets and supercells.

3. Ion-electron interaction: Modelled using a pseudo potential approach.

4. Ion-ion interactions

2.1 Electron-electron interactions

Most of the computational time in a total energy calculation will be spend in determining the energy contributions of the electron interactions. Firstly, thinking of electrons as charged particles, one would think the only contribution of these to the Hamiltonian would be their respective kinetic energy and a classical Coulomb repulsion. Nevertheless, the nature of electrons that must

obey certain rules under our system allow us to define two more special interactions that have a significant contribution to the total energy: *exchange* and *correlation*.

- **Exchange energy** As electrons obey the Pauli exclusion principle pawns from the anti-symmetric properties of the wave functions of the electrons (since they are fermions). The antisymmetry causes a spatial separation for electrons of the same spin, and this behaviour reduces the total energy. The acknowledgment of this interaction in the calculation is often referred as a Hartree-Fock approximation. Properly defined as:

$$E_x = -\int \psi_i(r)\psi_j(r')\frac{1}{|r-r'|}\psi_i(r)\psi_j(r')\,dr\,dr'$$

- **Correlation energy:** the total energy can be reduced once again if *opposite* spin electrons are also spatially separated. This difference is called *correlation energy* and it has proved to be difficult to calculate. Usually defined as the difference between the HF approximation and the exact quantum energy:

$$E_c = E_{tot} - E_{HF}$$

2.1.1 Hohenberg-Kohn theorems

Hohenberg and Kohn in 1964 [1] proved formaly that ehe whole system (including exchange and correlation energies) can be described in terms of the electron density (n) their article, they state the following theorems:

Theorem 1. *The total energy is an unique functional of the electron density $n(r)$.*

Theorem 2. *The ground state energy can be obtained variationally: the density that minimises the total energy is the exact ground state density.*

2.1.2 Kohn-Sham equation

In 1965, W. Kohn an L. J. Sham showed that we could change the many electron problem to an equivalent set of self consistent one electron equations.

The shape of the kohn-sham energy functional is

$$E[\psi_i] = 2\sum_i \int \psi_i \left[-\frac{\hbar^2}{2m}\right]\nabla^2\psi_i\,dr + \int V_{ion}(r)n(r)d^3r + \frac{e^2}{2}\int \frac{n(r)n(r')}{|r-r'|}d^3r\,dr' \tag{2.1}$$
$$+E_{XC}[n(r)] + E_{ion}(\{R_i\}).$$

Where the electron density is defined as:

$$n(r) \equiv 2\sum_i |\psi_i(x)|^2 \tag{2.2}$$

The equations that minimise this functional, are the self consistent solutions of the Kohn -Sham equations:

$$\epsilon_i\psi_i(r) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ion}(r) + V_H(r) + V_{XC}(r)\right]. \tag{2.3}$$

where ψ_i is the corresponding wave function of the electronic states i and ϵ_i is the KS eigenvalue. V_H is the Hartree potential, given by:

$$V_H(\boldsymbol{r}) = e^2 \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}^3 \boldsymbol{r}' \tag{2.4}$$

. The exchange-correlation functional y given by the functional derivative of the exchange-correlation energy.

$$V_{XC}(\boldsymbol{r}) = \frac{\delta E[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})} \tag{2.5}$$

2.1.3 General method

In order to solve the Kohn-Sham equations, the method need a trial electron density as a starting point. With it one can solve the KS-equations and find the electron wave functions. According to equation 2.2, one can easily calculate a new, and improved, electron density. One can compare the energies corresponding to each electron density. If the difference between them is less than a certain tolerance, then the ground state was found; if it is larger, the new electron density becomes the trial one, and the cycle continues until convergence is achieved.
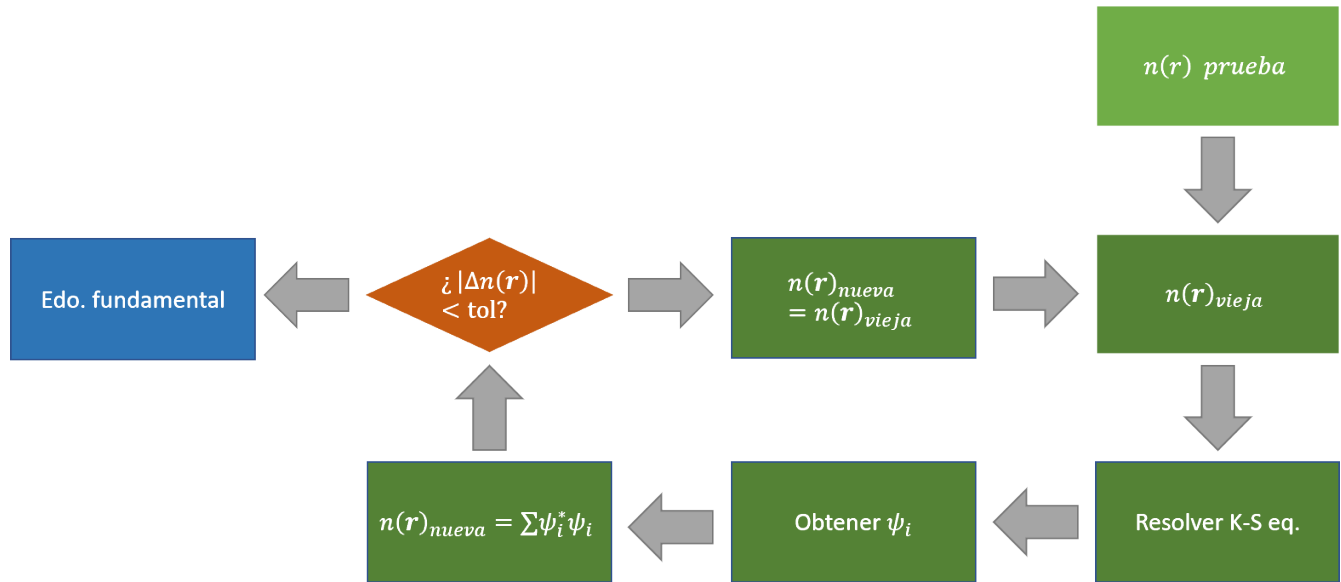

Figure 2.1: Representation of the self-consistent process for solving Kohn-Sham equations.

2.1.4 Approximations for the exchange-correlation functional: LDA

One of the simplest method for approximate the exchange-correlation energy is a method called the *local density approximation* or LDA. It states that the exchange correlation energy per electron at a point r of an electron gas is equal to the exchange-correlation energy per electron in a **homogeneous** gas that has the same density at the point r.

$$E_{XC}[n(\boldsymbol{r})] = \int \epsilon_{XC}\, n(\boldsymbol{r})\mathrm{d}^3 \boldsymbol{r} \tag{2.6}$$

$$\frac{\delta E[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})} = \frac{\delta E[n(\boldsymbol{r})\epsilon_{XC}(\boldsymbol{r})]}{\delta n(\boldsymbol{r})} \tag{2.7}$$

$$\epsilon_{XC}(\boldsymbol{r}) = \epsilon^{hom}XC(\boldsymbol{r}) \tag{2.8}$$

2.2   Periodicity and aperiodicity

2.2.1   Blochh's theorem and plane waves

From a theoretical background in solid state physics we know that we can approach a periodic system, by solving the problem in it's Wigner Seitz cell, or the minimum unit of repetition, utilizing the appropriated boundary conditions.

Bolch's theorem states that the electron wave function in a periodic solid is the product of a wave-like part and a cell periodic part (f_i). The first of them can be written in exponential form, a plane wave, dependent of the vectors in real space.

$$\psi_i(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} f_i(\boldsymbol{r}) \tag{2.9}$$

Then, the cell periodic part can be expanded in a basis of plane waves whose wave vectors are the reciprocal lattice vectors.

$$f_i(\boldsymbol{r}) = \sum_i c_{i,\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}} \tag{2.10}$$

The reciprocal lattice vectors are related to the regular lattice vectors (l) by the following equation. $\boldsymbol{G}\cdot\boldsymbol{l} = 2m\pi$ where m is an integer. Therefore, the electron wave function can be expanded in a basis of discrete plane waves as:

$$\psi_i(\boldsymbol{r}) = \sum_{\boldsymbol{G}} c_{i,\boldsymbol{k}+\boldsymbol{G}} e^{i\boldsymbol{k}\cdot\boldsymbol{G}} \tag{2.11}$$

In principle, this basis set if infinite. However, the coefficients of the waves with small kinetic energy are generally more important. For that reason it is convenient to truncate the basis set at an arbitrary energy, called **cutoff energy**. This combined with the fact that the plane waves are discrete (not continues) make the problem capable to be performed computationally.

Naturally, this truncation makes our result not exact. A large cutoff energy would make the error smaller, and our result more precise, at a cost of computational power or more time.

2.2.2   Plane wave representation of the Kohn-Sham equations

One other advantage of working with a basis of plane waves is that the KS-equations acquire a simpler form. By combination of equations 2.11 and 2.3, we can obtain the following equivalent

equations.

$$\sum_{G'} \left[-\frac{\hbar^2}{2m} |k + G|^2 \delta_{GG'} + V_{ion}(G - G') + V_H(G - G') \right.$$

$$\left. + V_{XC}(G - G') \right] c_{i,k+G'} = \epsilon_i c_{i,(k+G)} \tag{2.12}$$

2.2.3 Aperiodicity, supercells, and surfaces

Bolch theorem can not be used in non periodic systems. Examples are crystals that contain defects or in the direction perpendicular to a surface. An infinite number of plane waves would be required for modelling those kinds of systems. Thee only solution that avoids this problem is to make use of a supercell. A supercell become the new unit that will be repeated through space. Inside it we can model the defect surrounded by a bulk of crystal, the approximation will be better if we increase the size of the supercell until it converges.

One can construct supercells to treat problems like surfaces or even single molecules in x a similar manner.

2.3 Ion-electron interactions

2.3.1 Pseudopotential approxiamtion

2.4 Ion-ion interactions

2.5 Broyden–Fletcher–Goldfarb–Shanno algorithm

BFGS quasi-newton algorithm, based on the trust radius procedure, for structural relaxation

3 Computational Method

4 Results

5 Conclusions

Bibliography

[1] Pierre Hohenberg and Walter Kohn. "Inhomogeneous electron gas". In: *Physical review* 136.3B (1964), B864.