Magnetism of Cr Impurities Embedded in Cu fcc Matrix: Density Functional Calculations

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Abstract: We present extensive first principles density functional theory (DFT) calculations dedicated to analyze the magnetic properties of Cr n (n = 2 and 3) impurities embedded in a Cu fcc matrix. We consider several dimers and trimers having different interatomic distances. In all cases the Cr atoms have been embedded as substitutional impurities in the metallic network. For the case of the dimers we have considered two magnetic configurations: Ferromagnetic (Antiferromagnetic) when the atomic magnetic moments are parallel (antiparallel) each other, for this case we have found that the lowest-energy state corresponds to the antiferromagnetic coupling between Cr atoms whose interatomic distance is \( \sqrt{2} \). In the case of the Cr trimers we have considered three or four magnetic configurations, depending on the Cr impurity geometry, for this case we have found that the lowest-energy state corresponds to the antiferromagnetic Cr trimer AF (\( \uparrow, \downarrow, \downarrow \)) forming an isosceles right angle triangle whose hypotenuse and legs length are \( \sqrt{2} \) and \( a \), respectively, with magnetic moments c (2) = 3.45/-3.32/3.45 \( \mu_B \).

Key words: Chrome impurity, density functional calculations, magnetism of nanostructures.

1. Introduction

The research on magnetic clusters is motivated for the potential technological applications in magnetic recording media, spintronic devices and nanoelectronics, as well as to understand the physical properties of atoms and molecules.

There are many experimental and theoretical studies that involve different elements embedded in different materials. One experimental study was carried out by Huttel et al. [1]. They studied V atoms embedded in a Cu matrix by means of XMCD. Félix-Medina et al. [2] performed a theoretical study using DFT for small V clusters embedded in a Cu fcc matrix. Baker et al. [3] studied Fe clusters embedded in an Ag matrix using synchrotron radiation. In a recent paper Baker et al. [4] studied Fe clusters embedded in a Cu_{x}Au_{1-x} fcc matrix.

Chromium is remarkable for its magnetic properties; it is the only element which shows antiferromagnetic order at room temperature (and below). Above 38 ºC, chromium becomes a paramagnetic state. Its half-filled valence configuration leads to a large magnetic moment and strong interatomic bond [5]. Chromium clusters have been studied extensively in various configurations: free (pure [6] and doped with other atoms [7]) and deposited (in magnetic [8, 9] and non-magnetic substrates [10, 11]). Also experimental work was carried out with free [12] and deposited clusters on gold [13].

In this study, we have used the density functional theory (DFT) approach together with pseudopotential approximation of the electron-ion interaction. All
calculations were performed with Quantum Espresso code. We put special emphasis on: magnetic properties, including the local magnetic moments and their kind of coupling, and the difference of total energy for various geometrical configurations.

The remainder of the paper is organized as follows. In section II, the used theoretical method for the calculations is briefly explained. In section III, the obtained results are presented and discussed in terms of the atomic spin magnetic moments and differences in total energies. Finally, section IV summarizes the main conclusions.

2. Theoretical Method

In the present work, we have used the Quantum-Espresso code [14], which is based on the DFT [15, 16]. In all our calculations we have used the Generalized Gradient Approximation of Perdew Burke Ernzerhof (GGA-PBE) [17]. The pseudopotentials [18] used were taken from the Quantum Espresso Distribution [19] with scalar relativistic calculations, exchange-correlation of Perdew Burke Ernzerhof (PBE), non-linear core corrections, semicore stated in valence, and ultrasoft pseudopotential of Rabe Rappe Kaxiras Joannopoulos [20]. The Cr and Cu pseudopotential files were obtained by using the electronic configuration for each atom [Ar] 3d$^4$ 4s$^2$ and [Ar] 3d$^{10}$ 4s$^1$, respectively. We have used a cutoff of 35 Ry for the plane waves expansion of the pseudowave functions (560 Ry for the charge density and potential). We have studied Cr impurities (dimer and trimer) embedded in a Cu fcc matrix. The Cu fcc matrix system is represented by a cell containing a total of 48 atoms (6 planes with 8 atoms per plane), Fig. 1.

The Cr atoms are located at ideal positions in the fcc crystal. The Monkhorst-Pack scheme was used to define the k points and the calculations for each cell were performed with a grid of $4 \times 4 \times 4$ mesh in k-space. We have done some tests with a grid of $5 \times 5 \times 5$ and $6 \times 6 \times 6$ mesh, and the values of the total energy and the magnetic moments were only 4% less than those reported here.

The cell parameter used for the calculations is $a_{\text{Cu}} = 3.61$ Angstroms. The impurities embedded in Cu are schematically represented in the Figs. 2 and 3. In Fig. 2 we show the Cr dimers. The respective interatomic distances for dimers are (in order of appearance): $a\sqrt{2}$, $a\sqrt{3}/2$, a, $a\sqrt{3}$, and $a\sqrt{2}$. The Cr trimers are represented in Fig. 3; the Fig. 3a represents an equilateral triangle whose sides are equal to $a\sqrt{2}$; Fig. 3b is an isosceles right angle triangle whose hypotenuse and legs are, respectively, a and $a\sqrt{2}$; Fig. 3c is a right angle triangle whose hypotenuse and legs measure $a\sqrt{3}/2$, $a\sqrt{2}$ and a, respectively; Fig. 3d shows a linear trimer whose interatomic distances are equal to $a\sqrt{2}$; Fig. 3e is an isosceles right angle triangle whose hypotenuse and legs measure, respectively, $a\sqrt{2}$ and a; Fig. 3f is a right angle triangle whose hypotenuse and legs measure $a\sqrt{3}$, a and $a\sqrt{2}$, respectively; and finally Fig. 3g represents an equilateral triangle whose sides measure $a\sqrt{2}$.

For the case of Cr dimers, we have considered two magnetic configurations (Fig. 2): FM and AF. The FM (AF) case is when both atomic magnetic moments are parallel (antiparallel) each other. For the case of Cr trimers, the atoms are sitted in such a way that one of the trimers forms a straight line, the other six trimers

![Fig. 1 Schematic representation of the crystal cell containing six planes with eight atoms per plane. (a) Top view. The black circles represent the first atomic plane whereas the red circles represent the next atomic plane which is separated $a/2$ from the first plane. (b) Side view. Six planes containing eight atoms per plane, $a$ represents the lattice parameter which is 3.61 Angstroms.](image-url)
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2. Obtained Results

In this section, we shall show and discuss the

![Fig. 2 Magnetic moments and stability of ferromagnetic and antiferromagnetic Cr2 impurities embedded in a Cu fcc matrix. The substituted Cr atoms are represented by filled circles whereas the Cu atoms are represented by open circles. DTE represent the energies of the metastable states with respect to the ground state denoted by 0.0. The magnetic moments on Cr atoms for the jth configuration are represented by $C(j) = \mu_1/\mu_1$.](image)

form two equilateral triangles, two isosceles right angle triangles and two right angle triangles, respectively.

We have considered the next magnetic configurations for trimers (Fig. 3): FM = $(1\uparrow, 2\uparrow, 3\uparrow)$, AF1 = $(1\uparrow, 2\downarrow, 3\uparrow)$, AF2 = $(1\uparrow, 2\uparrow, 3\downarrow)$ and in some cases AF3 = $(1\downarrow, 2\uparrow, 3\uparrow)$ or AF3 = $(1\uparrow, 2\downarrow, 3\downarrow)$, where the arrows represent the direction of the magnetization of the atom.

3. Obtained Results

In this section, we shall show and discuss the

![Fig. 3 Magnetic moments and stability of ferromagnetic and antiferromagnetic Cr3 impurities embedded in a Cu fcc matrix. The substituted Cr atoms are represented by filled circles whereas the Cu atoms are represented by open circles. DTE represent the energies of the metastable states with respect to the ground state denoted by 0.0. The magnetic moments on Cr atoms for the jth configuration are denoted by $C(j) = \mu_1/\mu_2$.](image)
results obtained for Cr dimers and trimers embedded in a matrix of Cu fcc. The results are shown in Fig. 2, for dimers, and Fig. 3 for trimers. In each figure the difference of Total Energy (DTE) is represented by DTE = ΔE (1)/ΔE (2) for dimers and DTE = ΔE (1)/ΔE (2)/ΔE (3)/ΔE (4) for trimers, where ΔE (j) represents the value of the DTE that correspond to the jth magnetic configuration (j = 1 for FM and j = 2, 3, 4 for AFM, with j = 4 for the trimers that are showed by Fig. 3c and 3f). The values of the atomic magnetic moments are shown by c(j) = μj/μ2 for the dimers, and c(j) = μj/μ2/μ3 for trimers, where j again represents the jth magnetic configuration.

For the case of Cr dimers immersed in a Cu matrix, the lowest-energy state corresponds to Fig. 2a with the antiferromagnetic coupling, interatomic distance equal to a/√2, and an atomic magnetic moment of 3.46/-3.46 μB.

The second lowest-energy state corresponds to the Cr dimer represented in the Fig. 2b, with an antiferromagnetic coupling, interatomic distance equal to a/√3/2, a DTE = 1.99 meV/atom and atomic magnetic moment of 3.56/-3.56 μB.

For the case of Cr trimers immersed in the Cu matrix the lowest energy state corresponds to the isosceles right angle triangle whose hypotenuse and legs are, respectively, a and a/√2, which is represented in the Fig. 3b, with an AF (↑, ↓, ↑) coupling and atomic magnetic moments 3.45/-3.32/3.45 μB.

The second lowest energetic state for the trimers is for the AFM trimer represented in Fig. 3d, with a DTE = 0.99 meV/atom and atomic magnetic moments equal to c(2) = 3.54/-3.31/3.54 μB.

The higher mean magnetic moments for the Cr dimer and trimer corresponds to the ferromagnetic coupling showed in Fig. 2e and 3g, respectively, with magnetic moments given by 3.69/3.69 μB and 3.73/3.73 μB, with a DTE of 4.23 meV/atom for the dimer and 9.00 meV/Atom for the trimer.

Ruiz-Diaz et al. [6] have studied free Cr clusters using Vienna ab initio simulation package [21, 22], they studied dimers, trimers, tetramers, pentamers and hexamer, using Local Spin Density Approximation of Vosko-Wilk-Nussair (LSDA-VWN) [23] and Generalized Gradient Approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [17]. With the aim of comparing our results with those of Ruiz-Diaz et al., we show the results in Figs. 4a and 4b and Fig. 5a and 5d for dimers and trimers, respectively. For the case of the Cr dimer Ruiz-Diaz et al. found that the Cr dimer behaves nonmagnetic when is calculated with LSDA-VWN and antiferromagnetic with GGA-PBE giving magnetic moments 2.0/-2.0 μB.

For the case of the trimers, Ruiz-Diaz et al. studied several geometries, and they found that the ground state corresponds to the right angle triangle with atomic distances 2.52/1.61/3.09 Angstroms when they used the LSDA-VWN and 2.52/1.48/2.93 Angstroms, with the GGA-PBE. The atomic magnetic moments are -0.52/0.87/4.43 μB and -1.83/2.18/4.44 μB for LSDA and GGA respectively. The second energetic state found by Ruiz-Diaz et al. corresponds to the linear cluster for GGA and isosceles triangle for the LSDA. The atomic distances for the LSDA are 2.71/2.71/1.47 Angstroms whereas the magnetic moments are 0.16/0.16/4.45 μB. For the case when they used GGA...
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Fig. 5  Magnetic moments (in μB) and interatomic distances (in angstroms) of Cr trimers, (a) Cr lowest energy obtained by Ruiz-Díaz et al. using GGA, (b) Cr first state obtained by Ruiz-Díaz et al. using GGA, (c) Cr lowest energy obtained by Ruiz-Díaz et al. using LSDA, (d) Cr first state obtained by Ruiz-Díaz et al. using LSDA, (e) Cr lowest energy with interatomic distances of Cu fcc matrix, (f) Cr first state with interatomic distances of Cu fcc matrix, (g) Cr lowest energy impurities embedded in a Cu fcc matrix, (h) Cr first state impurities embedded in a Cu fcc matrix.

the atomic distances 1.56/2.65 Angstroms and the magnetic moments -0.52/0.87/4.43 μB.

We can compare our results with the results of Ruiz-Diaz et al. In our results the atomic magnetic moments for the free dimers and free trimers are bigger than those reported by Ruiz-Diaz et al, this is due to the atomic distances between Cr atoms are bigger than those reported by Ruiz-Diaz et al. We have expected to find that the atomic magnetic moments for the dimmers and trimers are bigger for the free Cr.

Fig. 6  (color online) d-Local density of states (d-LDOS) for spin up (black) and spin down (red) in the case of the free Cr dimer and free trimer and embedded dimer and embedded trimer with lowest energy. Dashed line represents the Fermi level. (a) Cr2 lowest energy impurities embedded in Cu fcc matrix, (b) free Cr 2 lowest energy with interatomic distance of Cu fcc matrix, (c) Cr 3 lowest energy impurities embedded in Cu fcc matrix and (d) free Cr 3 lowest energy with interatomic distance of Cu fcc matrix.

Clusters than embedded Cr impurities, this due to the hybridization with Cu atoms. We show in Fig. 6 the calculated local density of states (LDOS) for the free Cr dimer and free trimer and embedded dimer and embedded trimer with lowest energy.

We see that the LDOS for the free dimer and trimer present a big peak below the Fermi level, this produce that the Cr magnetic moments are big and they are almost the saturation values. For the embedded dimer and trimer we see that the LDOS are almost flat, this is due to the hybridization with the neighbors Cu atoms.

4. Conclusions

We have developed a study based on first principles of Cr impurities embedded in a Cu fcc matrix. We have found that for the case of dimers the ground state corresponds to the dimer with shortest interatomic distance a/√2, with antiferromagnetic coupling between Cr atoms and magnetic moments equal to 3.46/-3.46 μB. For the second state there is a difference of energy equal to 1.99 meV/atom and a distance between Cr atoms equal to a√(3/2), and magnetic moments for the Cr atoms equal to
3.56/-3.56 $\mu_B$. For the case of the Cr trimers we found that the ground state corresponds to trimer with right angle isosceles triangle with atomic distances equal to $a/\sqrt{2}$, $a/\sqrt{2}$ and $a$, with magnetic moments 3.45/-3.32/3.45 $\mu_B$.

We have compared our results with those of Ruiz-Díaz et al. and found that the atomic magnetic moments for the free dimers and free trimers are bigger than those reported by Ruiz-Díaz et al, due to the distances between Cr atoms that are bigger than those reported by Ruiz-Díaz et al.

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