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A comparative study of local magnetic properties of vanadium and chromium adsorbed on graphite

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Abstract. Recently vanadium 3s core-level x-ray photoemission of freshly evaporated V clusters on graphite exhibited a satellite structure, which has been assigned to magnetic moments of V adatoms. More generally the condition for the appearance of local magnetism in the case of 3d metal atoms adsorbed on a graphite surface is still an open question. In this paper we extend a previous extra-orbital tight-binding electronic-structure model to the cases of V and Cr isolated adatoms upon graphite. The equilibrium position of an adsorbed atom is found with a Born–Mayer repulsive term and the energy levels are chosen so as to satisfy Friedel's screening rule. The Hartree–Fock approximation has been used for the determination of the onset of local magnetism on a V or a Cr adatom. We discuss our results for two closely related cases of early 3d transition metals on graphite, i.e. V and Cr.

1. Introduction

Graphite is one of the most commonly used substrate materials in scanning tunnelling microscopy (Binnig *et al* 1982) and atomic-force microscopy (Binnig *et al* 1986). In the latter case, for example, progress has been achieved, recently, with the help of molecular-dynamics simulations to determine the metallic tip–substrate interaction (Landman *et al* 1989). Similarly, the interaction energies between a sharp palladium tip, represented by an apex atom, and graphite have been studied on the basis of first-principles calculations (Tomanek and Zhong 1991, Zhong *et al* 1991). The general electronic-structure tends along the first-row transition metals adsorbed on graphite and, especially, the conditions for the appearance of local 3d magnetic moments are still open and fascinating questions.

In this paper we limit our theoretical study to the case of two early transition metals (vanadium and chromium), at the beginning of the adsorption process upon graphite, i.e. when isolated adatoms predominate. Next, within an extra-orbital tight-binding approach for the electronic structure and a Born–Mayer term for the repulsion, we study the stable (sixfold) hollow position of V or Cr on graphite, simply by extending our previous work for boron, carbon or nitrogen adatoms (Rakotomahevitra *et al* 1993) to the case of 3d elements. Then, with the help of the Hartree–Fock approximation, we investigate the onset of local magnetism on a V or Cr adsorbed atom in terms of the intrasite exchange integral J^{dd} between d electrons.

Several theoretical calculations have shown that 3d transition metals are magnetic when they exist as free atoms, but can become non-magnetic when they form solid materials. As far as V is concerned, it is well known that the normal bulk solid does not exhibit magnetism whereas an expanded solid does. However, the nature of the transition from

non-magnetic to magnetic behaviour with respect to volume has been a long-standing problem (Moruzzi 1986). Using a linear muffin-tin (LMTO) supercell method, Khan (1993) recently found a stable ferromagnetic phase in the case of an isolated monolayer of V(001) with a large magnetic moment of $3.5\mu_B$; he also found ferromagnetic order for a single V overlayer on silver (001) with a small magnetic moment of $0.23\mu_B$ per V atom. A similar result has been worked out by Bouarab *et al* (1992) and Mokrani *et al* (1992), i.e. the magnetism of V epitaxially grown on Ag(001) exhibits in-plane antiferromagnetism for one V monolayer. As a matter of fact, the prediction of magnetic order for a single overlayer of V on Ag(001) is a constant result of computational solid-state physics (Fu *et al* 1985, Fu and Freeman 1986, Gay and Richter 1986, 1987). However, disagreement remains about the type of spin alignment and the magnitude of the polarization (Fu *et al* 1985, Blügel *et al* 1989). From an experimental point of view, the situation is far less clear. Inverse photoemission spectroscopy (Drube and Himpsel 1987) as well as electron-capture spectroscopy (Rau *et al* 1988) pointed out that an overlayer of V on Ag(100) is ferromagnetic, whereas spin-polarized x-ray photoemission spectroscopy (XPS) (Stampanoni *et al* 1988) and surface magneto-optical Kerr-effect experiments (Fink *et al* 1990) showed no such evidence for magnetism. Nevertheless, contamination could be a possible source of disagreement between the previously considered experiments. As for V on graphite, Binns *et al* (1992) pointed out recently that the appearance of magnetic moments on V can be quenched after exposure to carbon monoxide pollutant; only for freshly evaporated V clusters on graphite did these authors find a satellite structure in the V 3s core-level XPS which they attributed to the presence of magnetic moments on the V adatoms.

In the case of pure Cr, it is well known that this metal is a classic example of an itinerant antiferromagnet, which orders magnetically below the Néel temperature, $T_N = 311$ K, with a low-temperature ordered moment of $0.59\mu_B$. However, no evidence for antiferromagnetic ordering of nanometre-sized crystalline grains of BCC Cr was observed in neutron-diffraction data taken at temperatures as low as 20 K (Fitzsimmons *et al* 1993). Nevertheless, using a tight-binding Hubbard Hamiltonian in the unrestricted Hartree-Fock approximation, Pastor *et al* (1989) found that antiferromagnetic behaviour of Cr bulk is already present for very small free clusters. Several years ago, a pair of first-nearest neighbours of Cr in a copper host was determined to be coupled antiferromagnetically (Parlebas 1974) (whereas a similar pair of V atoms was found to be less magnetic than an isolated V atom in Cu: Parlebas and Gautier 1974). Also, Fu *et al* (1985) found that a Cr monolayer supported on gold(001) is ferromagnetic with a moment of $3.7\mu_B$, whereas Allan (1991) determined an antiferromagnetic structure with a moment close to $3.6\mu_B$ for a Cr layer adsorbed on Ag(001). Core-level XPS measurements of the Cr 3s multiplet splitting by Newstead *et al* (1987) indicated a rapid reduction of the magnetic moment with the Cr coverage on Ag(100). (For details see also Krembel *et al* 1991, 1992, 1993.) In the case of graphite substrates, the electronic structure of small Cr clusters deposited onto clean graphite have been studied recently by means of Auger, valence XPS and electron energy-loss spectroscopies, but no question about magnetism has been addressed (Lozzi *et al* 1991). It is the absence of clear results on the magnetic properties of Cr and V (adsorbed on graphite) that prompts us to examine that question, at least at the elementary level of non-interacting adatoms.

The outline of the paper is as follows. In section 2, we extend a previous electronic-structure model of sp adatoms (Rakotomahevitra *et al* 1993) to the case of 3d transition-metal adatoms on graphite; our extra-orbital tight-binding scheme is essentially based on (i) electron sharing between adsorbate and substrate due to an appreciable hybridization, as well as its self-consistent screening in the sense of Friedel (1958); (ii) a Born-Mayer term for the repulsion of the adatom; then a total-energy calculation enables us to determine the

most stable position of a given transition-metal atom, at first, in the paramagnetic phase. In section 3, we use the Hartree–Fock approximation to find all the possible magnetic solutions for V and Cr and their corresponding moments in terms of the exchange integral J^{dd} ; for reasonable values of J^{dd} , we are able to exhibit the spin-polarized electronic structure of V and Cr adatoms. Finally section 4 is devoted to a few concluding remarks.

2. Equilibrium positions for V or Cr adatoms

The electronic structure of a transition-metal adatom is obtained by a realistic extra-orbital Anderson-type (1961) model, the Hartree–Fock approximation of which will provide the magnetic solutions in the next section. More precisely we consider a system consisting of an extra transition-metal atom (3d, 4s orbitals) adsorbed on a graphite surface (2s, 2p orbitals of C), the electronic Hamiltonian of which is given by (Coqblin and Blandin 1968)

$$H = \sum_{nk\sigma} \epsilon_k^{n\sigma} c_k^{+n\sigma} c_k^{n\sigma} + \sum_{m\sigma} \epsilon_A^{m\sigma} a^{+m\sigma} a^{m\sigma} + \frac{1}{2}(U^{dd} - J^{dd}) \sum_{mm'\sigma(m \neq m')} a^{+m\sigma} a^{m\sigma} a^{+m'\sigma} a^{m'\sigma} \\ + U^{dd} \sum_{mm'} a^{+m\uparrow} a^{m\uparrow} a^{+m'\downarrow} a^{m'\downarrow} + \sum_{lmR\sigma} V_{RA}^{lm} (c_R^{l\sigma} a^{m\sigma} + \text{HC}). \quad (2.1)$$

In (2.1) U^{dd} and J^{dd} are, respectively, the Coulomb and exchange interactions between 3d electrons, but in the present section, we are only interested in the paramagnetic solution of the considered Hamiltonian in order to perform a total-energy calculation. $\{\epsilon_k^{n\sigma}\}$ are the electronic eigenenergies of the pure graphite surface eigenstates $|nk\sigma\rangle$ with wave number k and spin σ , $\{c_k^{+n\sigma}\}$ being the corresponding creation operators; $c_R^{l\sigma}$ creates a ‘molecular’ state $|Rl\sigma\rangle$ at graphite surface site R , with l symmetry (Σ or Π from 2s and 2p C orbitals, according to Rakotomahevitra *et al* (1993)) and spin σ . The operator $a^{+m\sigma}$ creates a state $|Am\sigma\rangle$ at adsorption site A , with m symmetry ($m = s, xy, yz, zx, x^2 - y^2, 3z^2 - r^2$), spin σ and energy $\epsilon_A^{m\sigma}$. In (2.1) and for the hollow position of A , the summation on R is restricted to the six first neighbours of the hexagonal ring below A . Finally V_{RA}^{lm} labels the hopping integral hybridization between $|Am\sigma\rangle$ and $|Rl\sigma\rangle$. Let us just recall a few more details. The eigenenergies $\{\epsilon_k^{n\sigma}\}$ of (2.1) are deduced from a band-structure calculation of a basal-plan surface for a graphite bilayer (Rakotomahevitra *et al* 1993, McKinnon and Choy 1993). In our numerical application, within the tight-binding method, we considered 10 000 k -points in the reduced Brillouin zone (Rakotomahevitra *et al* 1992), only keeping the k -components parallel to the graphite surface. Our results for the graphite surface density of states (see figure 1 of Rakotomahevitra *et al* 1993) is in fair agreement with a recent ‘local density approximation’ calculation (Trickey *et al* 1992).

We first consider the paramagnetic case: $J^{dd} \rightarrow 0$ and U^{dd} implicitly incorporated in the Hartree approximation. The 4s and 3d energy level ($\epsilon_A^{s\sigma} - \epsilon_A^{d\sigma}$) separation of a V or Cr adatom, as well as the hopping integrals between the adatom and the graphite C neighbours, are obtained, as explained by Rakotomahevitra *et al* (1992, 1993), through atomistic calculations within a given configuration (for V, $3d^4 4s^1$ and for Cr, $3d^5 4s^1$; see Clementi and Roetti 1974). We focus our attention on the hollow position of an adatom above a hexagon of C atoms. The equilibrium height h_0 is determined by the minimum of the total adsorption energy (figure 1) arising from the band-energy contribution and the Born–Mayer repulsion, according for example to Rakotomahevitra *et al* (1993). In our model there is no free parameter left, since $\epsilon_A^{d\sigma}$ is then deduced from the Friedel sum rule. Based on our numerical results (figure 1), we found that a Cr adatom is more tightly bound to the surface ($h_0 = 1.12 \text{ \AA}$) than a V adatom ($h_0 = 1.36 \text{ \AA}$). This tendency might reflect the respective sizes of the 3d orbitals in Cr and V.

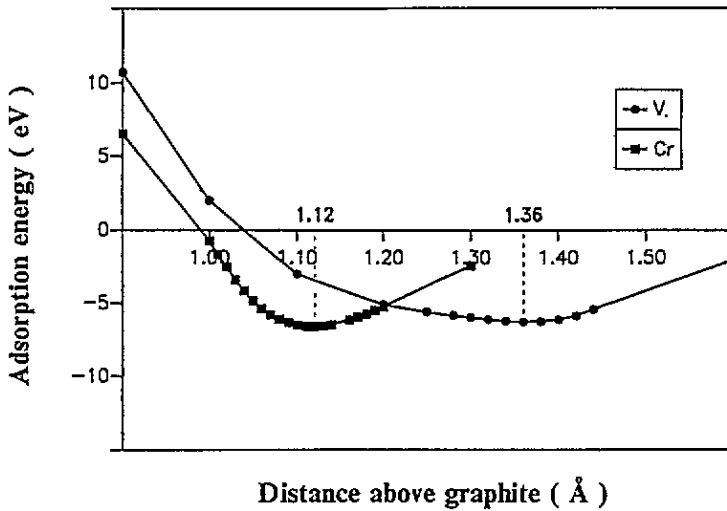


Figure 1. The total adsorption energy for V and Cr adatoms (hollow position) with respect to the distance from the graphite surface. The equilibrium position is 1.12 Å for Cr and 1.36 Å for V.

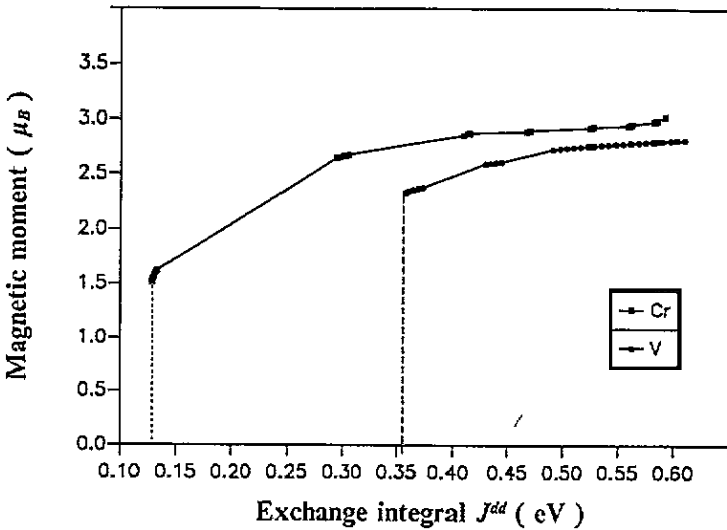


Figure 2. The Hartree-Fock magnetic moment versus J^{dd} for V and Cr.

3. Magnetic solutions for V and Cr adatoms

In the present model, we are concerned with the d polarization of the transition-metal adatom. Quite generally, the Hartree-Fock approximation of (2.1) can be written as follows (see Demangeat et al 1978, for example):

$$\epsilon_{HF}^{m\sigma} = \epsilon_{at}^d + \alpha^m + U^{dd}[N_A^{d\uparrow} + N_A^{d\downarrow} - Z^d] - J^{dd}N_A^{d\sigma} \tag{3.1}$$

where ϵ_{at}^d is the atomic level of the adatom and α^m the corresponding crystal field integral; m is now restricted to the d orbitals ($xy, yz, zx, x^2 - y^2$ and $3z^2 - r^2$); $N_A^{d\sigma}$ is the local

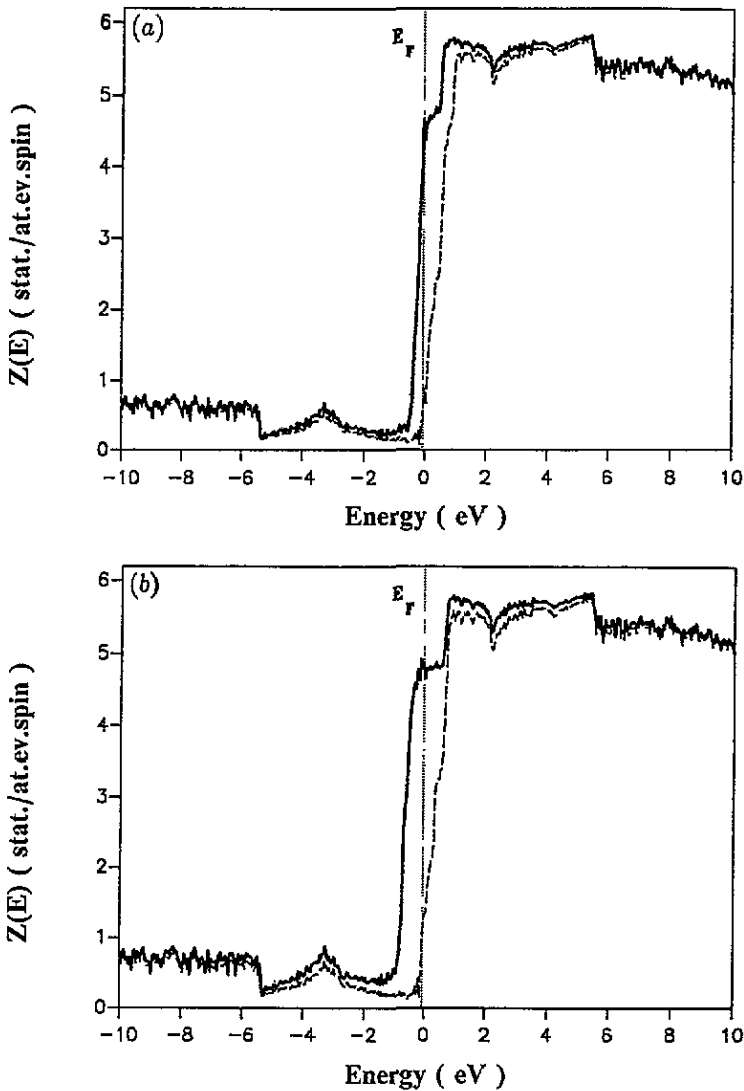


Figure 3. The spin-polarized total number of states $Z(E)$ for V (a) and Cr (b) adatoms: the full curve is for the majority spin and the dashed curve for the minority spin ($J^{dd} = 0.42$ eV for V and 0.56 eV for Cr).

electron number of symmetry d and spin σ at the A site; Z^d is the d -electron number initially brought by the adatom, and the quantity in square bracket indicates a possible d charge transfer at site A . If there is a local magnetic moment on A , it is defined by

$$\mu_A = N_A^{d\uparrow} - N_A^{d\downarrow}. \quad (3.2)$$

In fact, we solve (3.1) for $\epsilon_{HF}^{m\sigma}$, in a preliminary fashion and in the vicinity of the paramagnetic solution, E_A^d , obtained in section 2. Then (3.1) becomes

$$E^{d\sigma} = E_A^d - \sigma J^{dd} \mu_A / 2 \quad (\sigma = \pm 1). \quad (3.3)$$

Finally, we are able to plot (figure 2) the magnetic moment μ_A as a function of J^{dd} ($\mu_A = (E^{d\downarrow} - E^{d\uparrow})/J^{dd}$) for all the solutions satisfying the Friedel sum rule

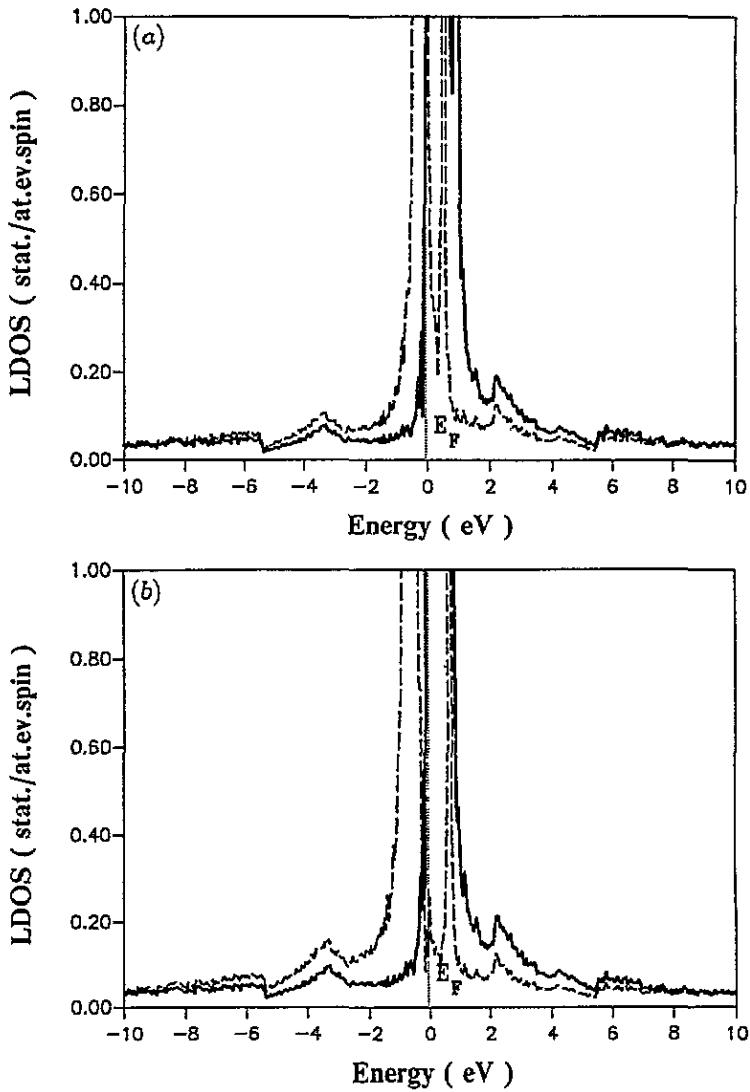


Figure 4. The spin-polarized LDOS at V (a) and Cr (b) adatoms: the dashed curve is for the majority spin and the full curve for the minority spin (same values of J^{dd} as in figure 3).

$(Z^{d\uparrow}(E_F) + Z^{d\downarrow}(E_F) + 2Z^s(E_F)) = 5$ for V and 6 for Cr). Also, to avoid unphysical solutions, we only keep the results leading to a fairly good neutrality on the adatom and its six C neighbours. From figure 2, we obtain a first-order transition for the onset of local magnetism at $J^{dd} = 0.13$ eV for Cr and 0.36 eV for V. Moreover, as expected, the saturation moment is a little larger for Cr (about $3\mu_B$) than for V. Then it is interesting to exhibit the spin-polarized electronic structure for a given J^{dd} of V or Cr (see table 1 of Stoeffler and Gautier (1990) where $J^{dd} = 0.42$ eV for bulk V and 0.56 eV for bulk Cr). Figure 3 shows the total number of states $Z(E)$ below energy E for both spin directions while figure 4 shows the local density of states (LDOS) per spin direction on the adatom site A with a magnetic moment of about $2.6\mu_B$ for V and $3.0\mu_B$ for Cr. Of course, for both spin directions, the main contribution to $Z(E)$ originates from the 3d states; a small

unpolarized contribution from the 4s states arises at about 0.5–1.0 eV above the Fermi level (figure 3). This last contribution shows up, again, as very narrow peaks in figure 4 at the same energies.

4. Conclusion

In the present paper we have studied the most stable hollow position of an early transition-metal adatom (V, Cr) on a graphite surface with a total adsorption-energy calculation (including a Born–Mayer repulsion term). Although our extra-orbital tight-binding approach for the band-structure contribution is rather elementary, we were sure to satisfy the Friedel sum rule, either in the paramagnetic or the ferromagnetic state. Moreover, for the spin-polarized solutions within the Hartree–Fock approximation, the best local neutrality (on the adatom and its first C neighbours) was used to avoid spurious results. As a consequence we were able to demonstrate a first-order transition for the onset of local magnetism at both V and Cr adatoms upon graphite. There are several interesting extensions of the present model: one extension would be to calculate in detail the 3s core-level x-ray photoemission spectra for adsorbed V and Cr in order to interpret the origin of the satellite structure (Binns *et al* 1992, Rakotomahevitra *et al* 1994); another extension would be to consider pairs of adatoms in order to discriminate between antiferromagnetic and ferromagnetic couplings as shown by Nait-Laziz *et al* (1993). Such developments are now in progress.

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