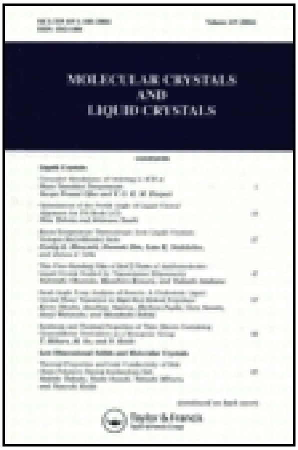

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MAGNETIC PROPERTIES OF VANADIUM ADSORBED ON GRAPHITE

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Abstract Recently V-3s core level XPS of freshly evaporated vanadium clusters on graphite exhibited the appearance of a satellite structure; the spectrum was then interpreted by the effect of surface magnetic moments on vanadium. In this paper we extend a previous electronic structure model calculation to the case of vanadium adatoms upon graphite with the help of the Hartree-Fock approximation. The outcoming results are used to discuss the origin of the satellite structure in V-3s core level XPS for a V-adatom upon graphite.

INTRODUCTION

Bulk solid vanadium does not exhibit magnetism whereas an isolated vanadium atom possesses a permanent magnetic moment of $3\mu_B$. Theoretically, magnetism is found in all calculations concerning adlayer of V on Ag(001) for example, although disagreement remains about the type of spin alignment and on the magnitude of the polarization [1–3]. Electron capture spectroscopy (ECS) measurements by Rau et al [4] pointed out that a monolayer of V on Ag(100) is ferromagnetic (even up to a thickness of 7 monolayers) whereas spin- polarized XPS and surface magneto-optical Kerr effect experiments [5] showed no such evidence for magnetism. However contamination could be a possible source of disagreement between the previously considered experiments. Recently Binns et al [6] pointed out that the appearence of magnetic moments on vanadium can be quenched after exposure to CO pollutant. However for freshly evaporated V clusters on graphite, these authors found a satellite structure in the 3s core level X-ray photoelectron spectrum (3s-XPS). A possible origin of the splitted structure of the spectra is the exchange coupling between the 3s core hole spin and the expected 3d magnetic moment on the same irradiated V surface atom [7]. Another origin of satellite (or another contribution to it) is just the 3s core hole effect on the 3d vanadium electronic states [7–9]. In this paper our purpose is twofolds: in section §1 we extend a previous electronic structure calculation of light atom in graphite [10] to the case of non-interacting vanadium adatoms upon graphite with the help of Hartree-Fock approximation; in section §2, the information contained in the outcoming densities of states is then used semi-quantitatively to build an impurity Anderson Hamiltonian which incorporate the various Coulomb interactions necessary to analyse the above mentioned 3s-XPS and its interpretation.

1. ELECTRONIC STRUCTURE OF A V ADATOM ON GRAPHITE

First we calculate the band structure of a basal-plan surface for a graphite bilayer within the tight-binding method as well as the corresponding Green's functions [11] . In our numerical application we consider 10000k-points in the reduced Brillouin zone [10] only keeping the k-components parallel to the graphite surface. Our results [11] for the graphite density of states (DOS) is in fair agreement with a recent 'local density approximation' calculation [12].

Next the extra-orbital Hamiltonian for an adatom A of vanadium on graphite is written as follows for a spin direction:

$$H^\sigma = H^0 + \sum_m \varepsilon_A^{m\sigma} a^{+\,m\sigma} a^{m\sigma} + \sum_{lmR} V_{RA}^{lm}(c_R^{+\,lm} a^{m\sigma} + h.c.) + \sum_{lR} v_R^l c_R^{+\,l\sigma} c_R^{l\sigma} \tag{1}$$

where H^0 is the pure graphite surface Hamiltonian; $a^{+\,m\sigma}$ creates a state $|Am\sigma>$ at adsorption site A, with m symmetry (m = s, xy, yz, zx, $x^2 - y^2, 3z^2 - r^2$), spin σ and energy $\varepsilon_A^{m\sigma}$; $c_R^{+\,l\sigma}$ creates a state $|Rl\sigma>$ at graphite surface site R, with l symmetry (Π or Σ from 2p and 2s carbon orbitals) and spin σ; V_{RA}^{lm} labels the hopping integral hybridization between $|Am\sigma>$ and $|Rl\sigma>$ whereas v_R^l designates a small perturbation potentiel at R near A due to the adsorption phenomenon. The Hartree-Fock expression of $\varepsilon_A^{m\sigma}$ is:

$$\varepsilon_A^{m\sigma} = \varepsilon_{at}^m + \alpha^m + U^{mm}[N_A^{m\uparrow} + N_A^{m\downarrow} - Z^m] - J^{mm} N_A^{m\sigma} \delta_{md} \tag{2}$$

where ε_{at}^m is the atomic level of the adatom; α^m the corresponding cristalline field integral; U^{mm} and $J^{mm}\delta_{md}$ are the effective mm Coulomb and dd exchange integrals; $N_A^{m\sigma}$ is the local electron number of symmetry m and spin σ at the A site ; Z^m is the m electron number initially brought by the adatom, and the quantity between brakets means the possible m charge transfer at A site. If there is a magnetic moment on A it is defined by $\mu = N_A^{d\uparrow} - N_A^{d\downarrow}$.

The 4s and 3d energy level separation in the case of paramagnetic vanadium adatom (fig.1a) as well as the hopping integrals between the adatom and the graphite carbon neighbours are obtained through atomistic calculations, taking into account a given configuration [13] (for V: $3d^4 4s^1$) and a given crystallographic position (hollow) of the adatom. This last position at equilibrium is obtained by finding the minimum of the total adsorption energy arising from the Born-Mayer repulsion and the band energy contribution [11] . Morever $\varepsilon_A^{m\sigma}$ and v_R^l are determined from the Friedel sum rule and from the local neutrality condition on the cluster VC_6 built from the V adatom and its six carbon neighbours. The magnetic solution (fig.1b) is then deduced from the above mentionned Hartree-Fock equation (2) and at the paramagnetic equilibrium height $h_o = 1.51$ Å upon the graphite surface.

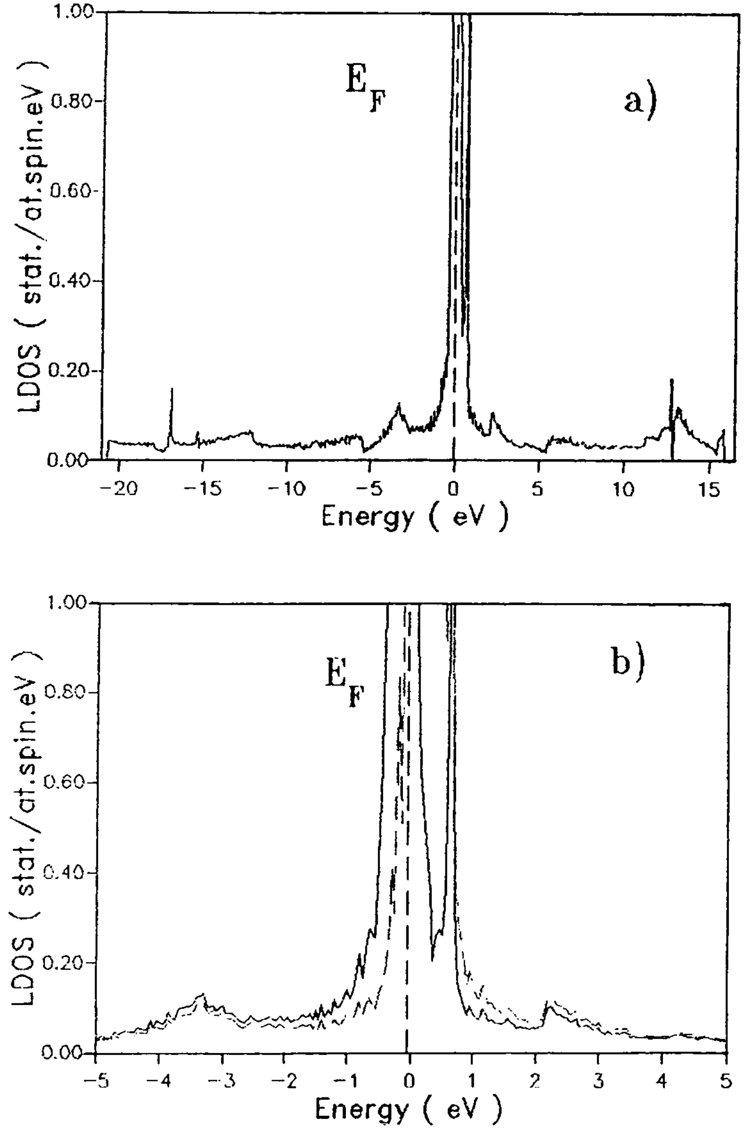

FIGURE 1: Local density of states (LDOS) of a vanadium adatom upon graphite: (a) paramagnetic and (b) magnetic solutions. In order to vizualize the magnetic splitting we have focused on LDOS near the Fermi level: Full curve is for majority spin and dashed line for minority spin.

2. CORE PHOTOEMISSION AT A V ADATOM ON GRAPHITE

According to Binns et al [6] the origin of the splitting in their 3s-XPS is the exchange coupling between the core hole spin $\vec{s}_c$ and the V-3d electron spin $\vec{S}$ at the V core hole site i.e. $-2J\vec{s}_c \bullet \vec{S}$ (see ref. 7). In the final state we obtain the multiplets with the total spin $S+1/2$ and $S-1/2$ and it is well known that the 3s photoelectron spectrum splits then into two peaks [7] with the intensity ratio $(S+1)/S$. For example, even if we take $S=3/2$ for V in the atomic $3d^3 4s^2$ configuration [13], the intensity ratio becomes 5/3, a result which seems far from the experimental one.

Another interpretation of the V 3s-XPS satellite obtained by Binns et al [6] is just the core hole effect upon the V-3d states [7-9]. It is then possible to use a simplified version of the previously considered V electronic structure on graphite as well as the filled band Anderson Hamiltonian [8-9] in order to express the 3s-XPS intensity (fig.2). The impurity Anderson model may not be appropriate for V clusters with delocalised V-3d electrons, because the effect of multi V sites may be important. However, as we will see next, in the final state of 3s-XPS, the 3d electrons should be more localised because of the core hole potential, so that the impurity model seems well to be applicable to the analysis of the considered spectrum. In the ground state, the Hamiltonian is written as:

$$H_g = \sum_{k\sigma} \varepsilon_k c_k^{+\sigma} c_k^{\sigma} + \varepsilon_A^d \sum_{\sigma} a^{+d\sigma} a^{d\sigma} + V^{hyb} \sum_{k\sigma} (c_k^{+\sigma} a^{d\sigma} + h.c.) + U^{dd} a^{+d\uparrow} a^{d\uparrow} a^{+d\downarrow} a^{d\downarrow} \quad (3)$$

where ε_k and ε_A^d are the energies of the filled graphite states and the adsorbed V 3d-level respectively; $c_k^{+\sigma}$ and $a^{+d\sigma}$ are the electron creation operators in the corresponding $|k\sigma>$ and $|Ad\sigma>$ states. Here k denotes the index of energy level ($k = 1, \ldots, N$) in the filled graphite band and σ specifies the spin as in eqs (1) and (2). In the present simplified model, only spin degeneracy is considered for the V atom whereas orbital degeneracy is disregarded so that only d^0, d^1 and d^2 configuration are considered. However an extension to a full N_d spin orbital degeneracy is straightforward [14], but the essential features of the spectrum do not change much provided that $N_d(V^{hyb})^2$ is kept constant [8]. The Hamiltonian used in eq (3) is based on a broken translational symmetry for the 3d-states of the V adatom (3d-single site model). Such an approximation is expected to make sense if the dipersional character of the V d-bandwidth is small as it should be for the case of a small V cluster on graphite and in the final state as already mentioned. Eq (3) simply treats the V 3d-states as localised states at a surface formed by the itinerant graphite electronic states: U^{dd} is the Coulomb repulsion interaction between 3d electrons at the adsorption site A and the hybridization V^{hyb} between V-3d and graphite states corresponds to an average of V_{KA}^{lm} in eq (1). In the final state of 3s-XPS, a 3s core hole is created and the V-3d level ε_A^d pulled down to $\varepsilon_A^d - U^{dc}$ by the core hole potential U^{dc} which acts like a localised impurity potential. The Hamiltonian is just:

$$H_f = H_g - U^{dc} \sum_{\sigma} a^{+d\sigma} a^{d\sigma} \quad (4)$$

Let us recall that in the case of the assumed filled graphite band, it is easy to derive exact solutions of the preceding one or at most two-particule Hamiltonians (3) and (4) (see refs 8 and 9). The spectrum of 3s-XPS is represented by:

$$F(E_B) = \sum_f |<f|g>|^2 (\Gamma/\pi)[(E_B - E_f + E_g)^2 + \Gamma^2]^{-1} \qquad (5)$$

where $|g>$ is the ground state of H_g with energy E_g and the $\{|f>\}$'s are the eigenstates of H_f with energies $\{E_f\}$; E_B is the electronic binding energy and Γ denotes the spectral broadening corresponding to the lifetime of the core hole, as well as experimental resolution. Finally we report (fig.2) our numerical results deduced from eq (5) within the following parameter values: U_{dc} = 4 eV; U_{dd}= 1.5 eV; V^{hyb} = 2.5 eV; Γ = 1.2 eV; the band width W of the filled graphite electronic states is W = 5 eV; N = 8 gives already a very good convergence; the charge transfer energy Δ between ε_d^0 and the centre of the filled band is Δ = 2.5 eV. Of course this set of parameter values is not unique but the corresponding 3s-XPS intensity provides a fairly good fit to the experimental result obtained by Binns et al [6] after background substraction and for V clusters on graphite (see their fig.3).

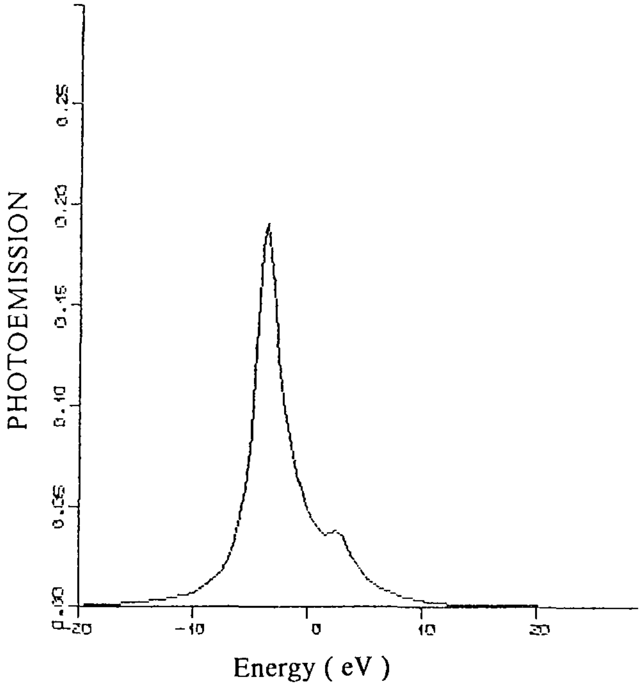

FIGURE 2: Calculated 3s-XPS of V upon graphite

CONCLUSION

In this short paper we have shown that it is possible to exhibit within Hartree-Fock approximation a magnetic solution for a vanadium adatom upon graphite. As far as the interpretation of the experimental 3s-XPS is concerned we think that the exchange coupling between the core hole spin and the V-3d electron spin, as the main origin of the appearance of a satellite, is questionable. Meanwhile we recall another basic mechanism to explain satellite structure, i.e. the core hole Coulomb effect upon the 3d states, which seems to be in a good accord with the result of Binns et al [6] for 3s-XPS of vanadium upon graphite.

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