ROLE OF ELECTRON CORRELATIONS AND MAGNETISM IN THE STABILITY OF Re DIMERS ON W(110)

A. M. Oleś*, M. C. Desjonquères ⁽¹⁾, D. Spanjaard ⁽²⁾ and G. Trégia ⁽²⁾

⁽¹⁾ IRF/DPhG/PAS-CEN de Saclay, F-91191 Gif-sur-Yvette, France

⁽²⁾ Laboratoire de Physique des Solides, Université Paris-Sud, Centre d'Orsay, F-91405 Orsay, France

Abstract. – We study the importance of electron correlations and magnetism in the stability of Re dimers on W(110) surface. It is found that the magnetism of monomers is the principal reason for the instability of Re₂ and that both monomer and dimer are magnetic.

1. Introduction

It is rather surprising that two Re atoms do not form a stable dimer on the W(110) surface, as found experimentally [1, 2]. One expects that the energy should be gained by new bond being formed between two single Re adatoms with a nearly half-filled 5d shell. Instead, the interaction between them is weak and repulsive at short distances [2, 3]. Furthermore, the decrease of this interaction energy is found along 5d series from Ta₂ to Re₂, followed by a slight increase from Re₂ to Pt₂ [2]. Clearly, the situation of Re₂ is unique and the key to understand the observed behaviour.

It has been suggested recently that the instability of Re₂ may be caused either by electron correlation [4], or by magnetic moments which form on Re₁ [5]. Both phenomena should destabilize Re₂. So far, they were treated separately: correlation effects within second order perturbation expansion (SOP) and magnetic instability within Hartree-Fock (HF) approximation. It has been found [4] that electron correlations are considerable and one expects that SOP is not sufficient [6]. One cannot also conclude about the nature of the ground state by making HF analysis. Motivated by these facts, we performed a model study of the Re₂ instability on W(110) treating local correlations by the method of *local ansatz* (LA), developed earlier for magnetism of transition metals [7].

2. Model Hamiltonian and calculation method

We study a model Hamiltonian [7]

$$H = \sum_{m i \sigma} \varepsilon_m n_{m i \sigma} + \sum_{m n i j \sigma} t_{m i, n j} a_{m i \sigma}^+ a_{n j \sigma} + \frac{1}{2} \sum_{m i j \sigma \sigma'} (U_m n_{m i \sigma} n_{m j \sigma'} + J_m a_{m i \sigma}^+ a_{m j \sigma'}^+ a_{m i \sigma} a_{m j \sigma'}), \quad (1)$$

where five equivalent 5d orbitals (*i, j*) at each atom *m* (*n*) are assumed. The corresponding local densities of states (LDOS) are found from a continued fraction expansion exact up to the 22nd moment and terminated in the usual way [8]. Thereby, we use the

neutrality condition for each atom to determine the site energies ε_m and assume that all W atoms of the W(110) surface are nonmagnetic. U_m and J_m stand for local Coulomb and exchange interaction, respectively. We found that it is sufficient to consider $U_{Re} = U_W = U$ and $J_{Re} = J_W = J$. Furthermore, we fix the exchange interaction by $J/U = 0.2$ which leaves only one free parameter U .

Electron correlations are treated within the LA in which the correlated ground state $|\psi_0\rangle$ is obtained from the corresponding HF state $|\phi_0\rangle$ as follows

$$|\psi_0\rangle = \exp \left[- \sum_n \eta_n O_n \right] |\phi_0\rangle. \quad (2)$$

The variational parameters η_n are found by the minimization of the ground state energy $E_{LA} = \langle \psi_0 | H | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle$. For the local operators O_n we use $n_{mi} n_{mj}$ and $n_{mi} n_{mj}$ to reduce charge fluctuations within orbital *i* and between two orbitals *i* and *j*, respectively, while the operators $s_{mi} s_{mj}$ introduce spin-spin correlations. We calculate the ground state energy E_{LA} by performing a variational second order expansion in powers of η_n . The respective quantities $\langle O_n H \rangle$, $\langle O_n H O_n \rangle$ and $\langle O_n O_n \rangle$ are evaluated by making use of the so-called $R = 0$ approximation in which only the leading local terms are preserved. This scheme allows to treat also stronger correlated systems and gives the correct atomic limit. More details may be found in reference [7].

We calculate the total energies of Re₁ and of Re₂ on W(110) for the respective geometries presented in figure 1. First, we solve the HF problem resulting from

Fig. 1. – Schematic geometry of Re₁ and Re₂ (empty circles) on W(110) (full circles).

* Permanent address: Institute of Physics, Jagellonian University PL-30059 Kraków, Poland.

(1) for different values of the magnetic moment M_m (at Re_1) and M_d (at one atom of Re_2). Thereby, the LDOS at two neighbour W atoms to the considered Re, indicated in figure 1 by a, b and α , β , respectively, are determined selfconsistently. The HF energies are defined as follows

$$E_{\text{HF},m} = E_{\text{HF}}(1) + 2E_{\text{HF}}(a) + E_{\text{HF}}(b) - 3E_{\text{HF}}(W), \quad (3)$$

$$E_{\text{HF},d} = E_{\text{HF}}(2) + E_{\text{HF}}(\alpha) + E_{\text{HF}}(\beta) - 2E_{\text{HF}}(W), \quad (4)$$

where $E_{\text{HF}}(1)$ and $E_{\text{HF}}(2)$ are the energies calculated for one Re atom in Re_1 and Re_2 and $E_{\text{HF}}(W)$ is the reference energy of W atom at W(110). Thereby, we assume that W_b and W_γ atoms connected by a bond with a single Re atom are equivalent. Next, we determine the correlation energies $E_{\text{corr},m}$ and $E_{\text{corr},d}$, defined in a similar way to equations (3, 4). Finally, the binding energy of Re_2 is

$$E_0 = E_{\text{HF},m} + E_{\text{corr},m} - E_{\text{HF},d} - E_{\text{corr},d} - E_{\text{rep}}. \quad (5)$$

The repulsive energy involved in the formation of Re - Re bond is $E_{\text{rep}} = 0.31$ eV [4].

3. Results and discussion

The main results of our study are summarized in figure 2. In the HF approximation Re_2 becomes unstable at $U \approx 2.3$ eV. Such a behaviour was already predicted earlier; at present we removed some inconsistency in the previous treatment of $E_{\text{HF},d}$. After adding correlations, the value of E_0 is somewhat reduced in non-magnetic states (for $U \leq 1.3$ eV), but this reduction does not exceed 0.1 eV and is far too small to destabilize Re_2 . In the region of magnetic Re_1 , the value of E_0 decreases faster and becomes negative at $U \approx 3.3$ eV. We find there $M_m > M_d$, so one gains more magnetic energy for Re_1 than for Re_2 . On the contrary, the gain from electron correlation is larger in less magnetic states of Re_2 . Thus, the correlation energy works *against* the dominating magnetic energy, i.e. *stabilizes* Re_2 .

Fig. 2. - (a) Magnetic moments M_m and M_d and (b) binding energy E_0 of Re_2 found in HF (dashed lines) and with the LA (full lines) for different values of U .

Several aspects of the presented analysis deserve attention. Since electron correlations suppress magnetic states (see [7] and the references therein), it is extremely important to include the saturation effects in the correlation energy [6]. The correlation energies presented in figure 2 are only about 40 % of those obtained in SOP. Also, the Hund's-rule coupling J is crucial for getting a magnetic ground state [7]. Indeed, by assuming $J = 0$, one finds nonmagnetic solutions with stable Re_2 . Of course, there are still many effects which may influence our quantitative result. The most important correction to the calculated E_0 may come from a better treatment of the clusters formed by Re_1 and Re_2 and the surrounding W atoms. Further corrections are expected: (i) from the possible magnetic polarization of W atoms, (ii) from different local orientations of Re moments in Re_2 , (iii) due to the inaccuracy of E_{rep} , (iv) if the value of U_W would be determined separately (but we find it encouraging that $U_W \approx 3.4$ eV fits the values of the cohesive energy and bulk modulus) and (v) from the spin-orbit coupling. Work on this line is in progress.

Summarizing, we have presented the simplest model for the Re_2 instability on W(110), in which one may treat magnetism and electron correlations simultaneously. Our conclusion that *the magnetism of Re_1 is the principal reason for the Re_2 instability* is expected to be independent of all the details mentioned above. We hope that one should be able to understand also the observed behaviour of 5d adatoms on W(110) [1-3] by extending the presented analysis. It would be very interesting to perform experiments to detect local moments of these adatoms at low coverage.

Acknowledgment

We thank Prof. J. Friedel for many stimulating discussions. The financial support of the Polish Research Project CPBP 01.03 is acknowledged.

- [1] Tsong, T. T., *Phys. Rev. B* **6** (1972) 417.
- [2] Bassett, D. W., *Surf. Sci.* **53** (1975) 74.
- [3] Tsong, T. T. and Casanova, R., *Phys. Rev. B* **24** (1981) 3063;
Fink, H. W. and Ehrlich, G., *Phys. Rev. Lett.* **52** (1984) 1532.
- [4] Bourdin, J. P., Desjonquères, M. C., Spanjaard, D. and Friedel, J., *Surf. Sci.* **157** (1985) L345.
- [5] Bourdin, J. P., Desjonquères, M. C., Spanjaard, D. and Trégliat, G., *Surf. Sci.* **181** (1987) L183.
- [6] Oleś, A. M. and Chao, K. A., *Phys. Lett.* **89A** (1982) 420.
- [7] Oleś, A. M. and Stollhoff, G., *Phys. Rev. B* **29** (1984) 314.
- [8] Haydock, R., Heine, V. and Kelly, M. J., *J. Phys. C* **5** (1972) 2845.