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# Calculation of the orbital magnetic moments in fcc 3d–4d binary clusters: Co–Rh and Co–Pd

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## Abstract

The orbital magnetic moments ( $\langle L \rangle$ ) and spin moments ( $\langle S \rangle$ ) of mixed fcc  $\text{Co}_N\text{Pd}_M$  and  $\text{Co}_N\text{Rh}_M$  ( $N, M = 19, 24$ ) clusters are determined by using a self-consistent real-space tight binding method. In all cases considered,  $\langle L \rangle$  amounts to 20%–50% of the total magnetic moment  $M_z$  ( $M_z = 2\langle S_z \rangle + \langle L_z \rangle$ ). Moreover, the  $M_z$  are remarkably larger than the  $M_z(\text{Co})$  values of the single Co cluster, due mainly to the local spin moments  $\langle S_{iz} \rangle$  induced at the Pd and Rh atoms, which amount to about 20% of  $M_z$  ( $2\langle S_{iz} \rangle_{\text{Pd,Rh}} = 0.1\text{--}0.8 \mu_B$ ) and to a considerable enhancement of the orbital moments  $\langle L_{\text{Co}} \rangle$  at the Co atoms ( $\langle L_{\text{Co}} \rangle = 0.2\text{--}1 \mu_B$ ). These results are analysed from a local perspective.

## 1. Introduction

Investigations of orbital magnetism in low dimensional systems—on the way from the atoms to the solid—show that the local and average orbital moments  $L$  are very sensitive to the local atomic environment [1–8]. For example, calculations on transition metal (TM) surfaces have revealed an important enhancement of the local orbital moments  $L$  at the uppermost surface layers [7] and that  $L$  is in general larger at open surfaces than at more compact ones.

In the case of free clusters, very little is known about the local atomic environment dependence of orbital magnetism, particularly from the point of view of theory, which has been so far concerned mainly with the dominant spin contributions. Recent self-consistent calculations [8] of  $L$  in transition metal clusters show that reduction of the system size causes a remarkable enhancement of  $L$  with respect to the bulk.

These results lead us to anticipate interesting size and structural dependences of the orbital moments in other systems particularly in the case of 4d transition metal elements, which are non-magnetic in the bulk and show weak, non-saturated, cluster magnetism [9–13]. Moreover,

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mixed transition metal clusters formed with 3d and 4d elements such as Co–Pd and Co–Rh systems are particularly appealing due to the strong magnetic susceptibility of Pd and the appearance of weak, non-saturated magnetism in Rh clusters [9–13]. In addition, it has been shown that the interface of these binary systems plays a crucial role on their magnetic behaviour [14–16].

It is the purpose of this communication to present representative results for the orbital moments of Co–Pd and Co–Rh clusters in order to show their importance to the value of the total magnetic moment.

## 2. Theoretical method

We consider a self-consistent tight binding method developed in [7] and [17]. The electronic Hamiltonian is given by the sum of three terms:

$$H = H_0 + H_C + H_{SO}. \quad (1)$$

$H_0$  refers to the inter-atomic hopping term. The Coulomb interaction  $H_C$  is treated in the unrestricted Hartree–Fock approximation:

$$H_C = \sum_{im\sigma} \Delta\varepsilon_{im\sigma} \hat{n}_{im\sigma}, \quad (2)$$

where  $\hat{n}_{im\sigma} = \hat{c}_{im\sigma}^\dagger \hat{c}_{im\sigma}$  is the electron-number operator and

$$\Delta\varepsilon_{im\sigma} = \sum_{m'} \left( U_{mm'} - \frac{J_{mm'}}{2} \right) v_{im'} - \frac{\sigma}{2} \sum_{m'} J_{mm'} \mu_{im'} \quad (3)$$

is the site- and spin-dependent shift of the d level. Notice that the direct and exchange Coulomb integrals  $U_{mm'}$  and  $J_{mm'}$  depend on  $m$  due to the angular dependence of the atomic-like orbitals.  $U_{mm'}$  and  $J_{mm'}$  are expressed in terms of the three independent radial Coulomb integrals  $F^{(0)}$ ,  $F^{(2)}$  and  $F^{(4)}$  allowed by atomic symmetry [18]. These are chosen by taking the ratios. In this way atomic symmetry is strictly respected and all atomic Hund's rules are naturally derived [18]. The third term in equation (1) refers to the spin–orbit interaction [19]:

$$H_{SO} = -\xi \sum_{i,\alpha\sigma,\beta\sigma'} (\vec{L}_i \cdot \vec{S}_i)_{\alpha\sigma,\beta\sigma'} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{i\beta\sigma'}, \quad (4)$$

where  $(\vec{L}_i \cdot \vec{S}_i)_{\alpha\sigma,\beta\sigma'}$  are the intra-atomic matrix elements of  $\vec{L} \cdot \vec{S}$  that couple the up and down spin manifolds and depend on the orientation of the magnetization.

The local densities of electronic states (DOS)  $\rho_{im\sigma}^\delta(\varepsilon)$  are determined self-consistently for each orientation  $\delta$  of the spin magnetization  $\vec{S}$ . The associated single-particle problem is solved by using the Haydock–Heine–Kelly recursion method [20]. The spin and charge densities are obtained with an accuracy  $\epsilon \simeq 10^{-10}$  electrons/atom.

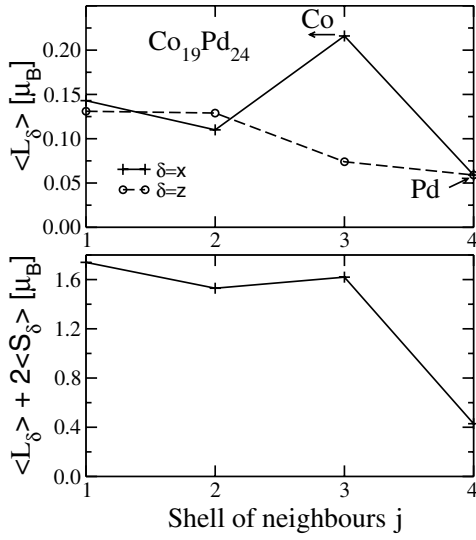
Once self-consistency is achieved, the average local orbital moments  $\langle L_{i\delta} \rangle$  at atom  $i$  are calculated from

$$\langle L_{i\delta} \rangle = \sum_{\sigma} \sum_{m=-2}^2 \int_{-\infty}^{\varepsilon_F} m \rho_{im\sigma}^\delta(\varepsilon) d\varepsilon, \quad (5)$$

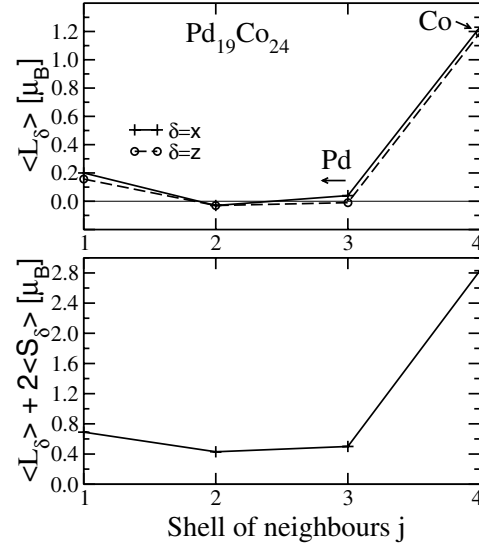
where  $m$  indicates the magnetic quantum number. The quantization axis of the orbital momentum is thereby taken to be the same as the spin quantization axis.

The electronic energy per atom  $E_\delta = (1/N) \sum_i E_\delta(i)$  can be written as the sum of local contributions:

$$E_\delta(i) = \sum_{m\sigma} \left[ \int_{-\infty}^{\varepsilon_F} \varepsilon \rho_{im\sigma}^\delta(\varepsilon) d\varepsilon - E_{im\sigma}^{\text{dc}} \right] \quad (6)$$



**Figure 1.** Local orbital magnetic moments along the spin magnetization direction and total magnetic moments in the easy axis ( $\langle L_\delta \rangle + 2\langle S_\delta \rangle$ ) in fcc-like  $\text{Co}_{19}\text{Pd}_{24}$  clusters. The results correspond to the average at each NN shell  $j$  surrounding the central atom  $j = 1$ .  $\delta = x, z$  indicate different spin magnetization directions as described in the text. The shells  $j \leq 3$  ( $j \geq 4$ ) correspond to Co (Pd) atoms. The lines are a guide to the eye.



**Figure 2.** Local orbital magnetic moments along the spin magnetization direction and total magnetic moments in the easy axis ( $\langle L_\delta \rangle + 2\langle S_\delta \rangle$ ) in fcc-like  $\text{Pd}_{19}\text{Co}_{24}$  clusters. The results correspond to the average at each NN shell  $j$  surrounding the central atom  $j = 1$ .  $\delta = x, z$  indicate different spin magnetization directions as described in the text. The shells  $j \leq 3$  ( $j \geq 4$ ) correspond to Pd (Co) atoms. The lines are a guide to the eye.

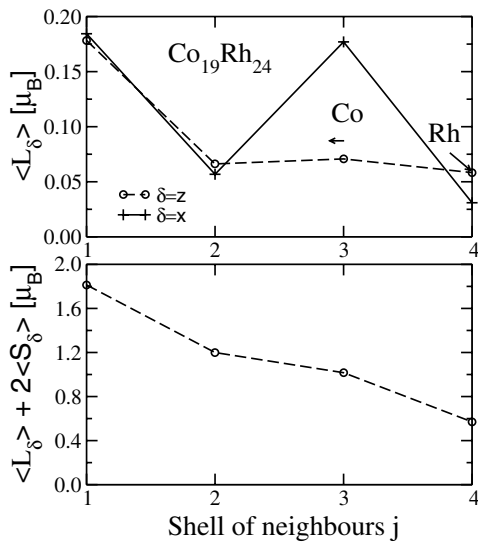
corresponding to the atoms  $i$  of the cluster. Here  $E_{im\sigma}^{\text{dc}} = (1/2)\Delta\varepsilon_{i\sigma}\langle\hat{n}_{im\sigma}\rangle$  stands for the double-counting correction. The magnetic anisotropy energy (MAE) is defined as the change  $\Delta E$  in the electronic energy  $E_\delta$  associated with a change in the orientation of the magnetization. Thus, positive (negative) values of the off-plane anisotropy energy  $\Delta E_{xz} = E_x - E_z$  indicate a perpendicular easy (hard) axis. Taking advantage of the local formulation one may express  $\Delta E_{xz} = \sum_i \Delta E_{xz}(i)$  as a sum of atom-resolved contributions:

$$\Delta E_{xy}(i) = E_x(i) - E_z(i), \quad (7)$$

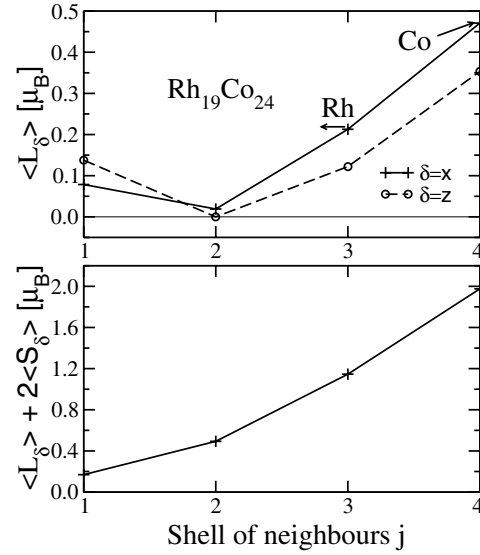
where the  $E_\delta(i)$  are given by equation (6). Thus, the magneto-anisotropic properties can be related to the various local atomic environments.

### 3. Results

In the present work we are ignoring structure optimization since the localized character of the d-electron states and the complicated dependence of the magnetic moments and magnetic order on the cluster structure have made the application of fully electronic geometry optimization procedures impracticable except for very small clusters. However, as suggested by experiment [12], we consider fcc-like 43-atom clusters formed by a central atom and its successive shells of nearest neighbours. For Co–Pd and Co–Rh this corresponds to a  $\text{Co}_{19}$  ( $\text{Pd}_{19}$ ,  $\text{Rh}_{19}$ ) core covered with a  $\text{Pd}_{24}$ ,  $\text{Rh}_{24}$  ( $\text{Co}_{24}$ ) shell. For the direction of magnetization  $\delta$ , we take  $\delta = z$ , usually along a principal  $C_n$  symmetry axis of the cluster, and  $\delta = x$  along a nearest neighbour (NN) bond perpendicular to  $z$ .



**Figure 3.** Local orbital magnetic moments along the spin magnetization direction and total magnetic moments in the easy axis ( $\langle L_\delta \rangle + 2\langle S_\delta \rangle$ ) in fcc-like  $\text{Co}_{19}\text{Rh}_{24}$  clusters. The results correspond to the average at each NN shell  $j$  surrounding the central atom  $j = 1$ .  $\delta = x, z$  indicate different spin magnetization directions as described in the text. The shells  $j \leq 3$  ( $j \geq 4$ ) correspond to Co (Rh) atoms. The lines are a guide to the eye.



**Figure 4.** Local orbital magnetic moments along the spin magnetization direction and total magnetic moments in the easy axis ( $\langle L_\delta \rangle + 2\langle S_\delta \rangle$ ) in fcc-like  $\text{Rh}_{19}\text{Co}_{24}$  clusters. The results correspond to the average at each NN shell  $j$  surrounding the central atom  $j = 1$ .  $\delta = x, z$  indicate different spin magnetization directions as described in the text. The shells  $j \leq 3$  ( $j \geq 4$ ) correspond to Rh (Co) atoms. The lines are a guide to the eye.

For the  $\text{Co}_{19}\text{Pd}_{24}$  cluster the total magnetic moment per Co atom  $M_\delta$  is remarkably large ( $M_z = 2.22 \mu_B$ ) [21]. This is mainly due to the contributions to  $M_\delta$  of the local spin moments induced at the Pd atoms of the Co–Pd interface ( $2\langle S \rangle_{\text{Pd}} = 0.30\text{--}0.35 \mu_B$ ) and to the enhanced orbital magnetic moments  $\langle L_\delta \rangle$ , which are always parallel to the spin moments. The calculated average orbital moment per Co atom is  $\langle L \rangle = 0.23 \mu_B$ . Note that these values are enhanced by about 100% with respect to the Co bulk orbital moment.

The environment dependence of the local orbital moments  $\langle L_\delta \rangle(j)$  provides further insight into the magnetic behaviour [8]. Figure 1 displays  $\langle L_\delta \rangle(j)$  for  $\text{Co}_{19}\text{Pd}_{24}$ , where  $j = 1$  refers to the central atom and  $j > 1$  to the successive NN shells. The sites  $j \leq 3$  ( $j \geq 4$ ) correspond to the Co (Pd) atoms. One observes that  $\langle L_\delta \rangle(j)$  generally increases with  $j$ , showing some oscillations as we move from the centre to the surface of the cluster. Notice the particularly large value of  $\langle L_x \rangle(3)$  which corresponds to the Co atoms at the interface:  $\langle L_x \rangle(j = 3) \simeq 0.23 \mu_B$ .

It is also interesting to consider a Co–Pd cluster formed with a Pd core. In figure 2 results are given for  $\langle L_\delta \rangle(j)$  and for the total magnetic moment along the easy axis  $M_\delta(j) = 2\langle S_\delta \rangle(j) + \langle L_\delta \rangle(j)$  for the  $\text{Pd}_{19}\text{Co}_{24}$  cluster. Notice that in this case, we take the bulk Pd NN inter-atomic distance. The increase in the NN distance affects mainly the orbital magnetic moment at the Co atoms. Indeed,  $\langle L_\delta \rangle(4) = 1.2 \mu_B$  and, as a consequence, an important enhancement of  $M_\delta$  is obtained (see figure 2).

Similar magnetic behaviour is observed in Co–Rh clusters (see figures 3 and 4). Also, in this case, the atoms in the interior of the clusters play a predominant role. In fact, if a Co core is assumed,  $M_\delta \simeq 1.8 \mu_B$  for  $\text{Co}_{19}\text{Co}_{24}$  and  $M_\delta \simeq 2.5 \mu_B$  for  $\text{Rh}_{19}\text{Co}_{24}$  having a Rh core. This is probably due to the important 3d–4d-electron hybridization of Co–Rh clusters being

more important in the case of clusters having a Co core since more Rh atoms are involved. In fact, here  $M_\delta$  is smaller. Furthermore, the value obtained for  $M_\delta$  for  $\text{Rh}_{19}\text{Co}_{24}$  is in agreement with recent experiments [12].

It is important to note that the Pd and Rh contributions amount to about 20% of the total moment per Co atom [ $\mu_{\text{Pd,Rh}} = \langle L_\delta \rangle_{\text{Pd,Rh}} + 2\langle S_\delta \rangle_{\text{Pd,Rh}} = (0.2\text{--}0.3) \mu_{\text{B}}$ ]. The orbital and spin moments at the interfaces are mainly responsible for this increase of  $\mu_{\text{Pd,Rh}}$ . These results demonstrate that it is the interface, rather than just the reduction of the local coordination number, which is responsible for the enhancement of the magnetic moments.

The anisotropy of  $\langle L_\delta \rangle(j)$  reflects the anisotropy of spin–orbit interactions from a local point of view. Our results show a significant  $\Delta L(j) = \langle L_x \rangle(j) - \langle L_z \rangle(j)$  with the largest values being found at the interface Co atoms (see figures 1–4). This is consistent with the large calculated MAE per Co atom  $\Delta E_{xz} = E_x - E_z$ . Indeed, the local contribution of the outermost Co shell in  $\text{Co}_{19}\text{Pd}_{24}$  and  $\text{Co}_{19}\text{Rh}_{24}$  to the MAE stabilizes the easy direction of the magnetization ( $\Delta E_{xz} < 0$  in  $\text{Co}_{19}\text{Pd}_{24}$  and  $\Delta E_{xz} > 0$  in  $\text{Co}_{19}\text{Rh}_{24}$  for  $j = 3$ ). Once more, these results indicate that the interface of Co–Pd and Co–Rh plays a main role in determining the stable magnetization direction of the system. In addition, a rich and complex environment dependence of  $\Delta E_{xz}$  is obtained by manipulating the interface. Replacing the Co core (Rh shell) by a Rh core (Co shell) changes the easy axis. Once again, the contribution of the local  $\Delta E_{xz}$  at the interface to the MAE stabilizes the direction of magnetization. The environment dependence of  $\Delta E_{xz}$  can be viewed as the result of two main contributions: the changes in the electronic structure of the Co cluster due to Co–Pd and Co–Rh hybridizations and the local MAE of the interface Pd and Rh atoms which carry small magnetic moments. Additional interesting magneto-anisotropic behaviour is expected if mixing of the 3d and 4d elements at the interface is allowed.

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