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Orbital moment of a single Co atom on a Pt(111) surface—a view from correlated band theory

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Abstract

The orbital magnetic moment of a Co adatom on a Pt(111) surface is calculated in good agreement with experimental data making use of the LSDA + U method. It is shown that both electron correlation induced orbital polarization and structural relaxation play essential roles in orbital moment formation. The microscopic origins of the orbital moment enhancement are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

According to Hund's rules, gas phase transition metal atoms possess large spin M_S and orbital M_L moments mediated by intra-atomic Coulomb interactions. In a solid, where electron delocalization and crystal field effects compete with Coulomb interactions, there is a substantial decrease in M_S and partial or total quenching of M_L .

Recent x-ray magnetic circular dichroism (XMCD) measurements [1] report M_S and M_L of Co adatoms and small Co clusters on Pt(111) in an ultra-high-vacuum. $M_L = 1.1 \pm 0.1 \mu_B$ and $M_S + 7M_D = 1.8 \pm 0.1 \mu_B$ (where M_D is a spin dipole moment) were evaluated from XMCD spectra using the conventional sum rules [2]. The number of holes in the Co atom 3d-manifold $n_d = 2.4$ was taken from local spin-density calculations (LSDA). The XMCD experiments are complemented by spin-polarized-relativistic Korringa–Kohn–Rostocker (KKR) Green's function LSDA theoretical calculations, and $M_S = 2.14 \mu_B$ and $M_L = 0.60 \mu_B$ for Co site were obtained. No structural relaxation of the Co atom position over the Pt surface was considered, and the atomic-sphere approximation was employed.

The authors of [1] assumed that the M_L discrepancy between the KKR–LSDA theory and the XMCD experiments originates from the lack of orbital polarization (OP) in LSDA. They used the well known orbital polarization correction of Brooks [3], adding to the LSDA total energy functional an ad hoc term $\frac{1}{2}B_R M_L^2$ with the LSDA calculated Racah parameter

B_R . This form of OP correction was widely used in the past to improve upon M_L in the bulk transition d- and f-metals where sometimes it works well [4].

For a Co atom on a Pt surface, Gambardella *et al* found out that the Brooks OP yields an M_L which substantially exceeds the experimental value. They had to reduce the LSDA calculated B_R by 50% in order to obtain a $M_L = 1.50 \mu_B$ comparable with the experimental XMCD data. It is assumed in [1] that the reduction of B_R compensates for a lack of structural relaxation.

In this work we explore another avenue for the orbital polarization correction to LSDA which is based on the correlated band theory LSDA + U method [5]. It consists of LSDA augmented by a correcting energy of a multiband Hubbard type and a 'double-counting' subtraction term which accounts approximately for an electron–electron interaction energy already included in the LSDA. Minimization of the LSDA + U functional generates not only the ground state total energy, but also one-electron band structure energies and spin–orbital states. The basic difference between the LSDA + U method and the LSDA is its explicit dependence on on-site spin and orbitally resolved occupation matrices. The LSDA + U method creates in addition to the spin-only dependent LSDA potential, the spin and orbitally dependent on-site '+ U ' potential which gives OP beyond that given by the LSDA (where it comes from the spin–orbit coupling only).

It was shown by Solovyev *et al* [6] that LSDA + U produces the correct OP for insulating 3d-oxides. Recent

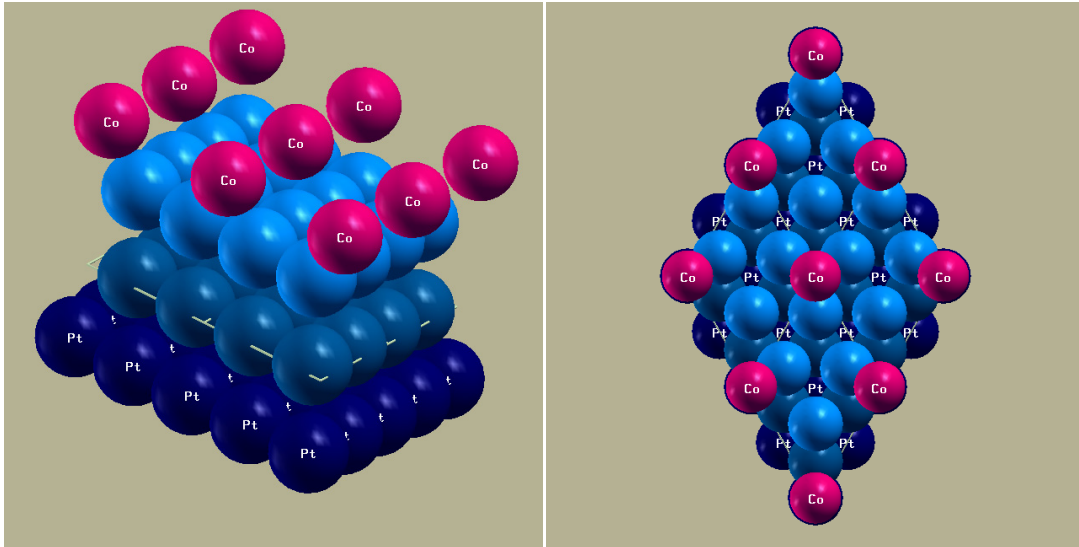


Figure 1. Schematic crystal structure of a model supercell: (left) general view, (right) top view with the Co adatom in the fcc position.

parameter-free GW calculations for transition metal based materials [7] produce OP which is very similar to LSDA + U results with the appropriate choice of Coulomb U [8].

2. Results and discussion

We performed supercell calculations to model a Co adatom at a Pt(111) surface. The supercell consists of three Pt(111) layers with a doubled ($p(2 \times 2)$) 2-dimensional unit cell, and the Co atom on the top is taken to be in the fcc position (see figure 1). The vacuum is modeled by the equivalent of two empty Pt layers. All in-plane interatomic distances are adopted to be those of pure Pt. The distance between the Co atom and the Pt surface was varied in the calculations. We note that while the chosen supercell is quite small, it provides separation of Co atoms beyond the second nearest neighbor distance and includes interaction of Co with first and second Pt nearest neighbors. Herein we assume that the given supercell is sufficient for Co M_L calculations, which is mainly a local quantity.

We use the LSDA + U method implemented in the full-potential linearized augmented plane-wave (FP-LAPW) method including spin-orbit coupling (SOC) [9, 10]. When SOC is taken into account, the spin is no longer a good quantum number, and the LSDA + U total-energy functional contains additional spin off-diagonal elements of the on-site occupation matrix $n_{m_1\sigma_1, m_2\sigma_2}$ [6]. The LSDA contributions to the effective potential (and corresponding terms in the total energy) are corrected to exclude the non-spherical interaction off the d-states. It helps to avoid the non-spherical Coulomb and exchange energy ‘double counting’ of d-states in LSDA and ‘+ U ’ parts of the effective potential and also corrects the non-spherical self-interaction of the d-states.

In the self-consistent calculations we used 48 special k -points in combination with a Gaussian smearing for the k -point weighting. A quasi-2D Brillouin zone (BZ) with $k_z = 0$ was adopted in order to simulate the 2D character of the problem,

notwithstanding that the supercell calculations themselves are inherently three-dimensional. The ‘muffin-tin’ radii used are $R_{MT} = 2.2$ au for Co and 2.5 au for Pt and $R_{MT}^{Co} \times K_{max} = 7.7$, with K_{max} the cut-off for the LAPW basis. The Coulomb $U = 2$ eV and exchange $J = 0.9$ eV were chosen which are in the range of commonly accepted values for 3d-metals. In principle, U can be calculated by a linear-response LSDA procedure [11] or from GW [7], both yielding the values ~ 2 eV. As for exchange J , it is not affected by solid-state screening and is equal to the LSDA calculated Stoner exchange parameter. The spin quantization axis is fixed along the out-of-plane z -direction.

First let us make a comparison with the results of KKR for unrelaxed geometry (see table 1). The LSDA calculated values for M_S and M_L agree quite well. However, the M_L per d-hole is somewhat bigger in KKR than in FP-LAPW calculations since d-shell occupation is greater in KKR (7.6) than in FP-LAPW (7.2). This is probably due to the difference in the radius of atomic sphere approximation (ASA) spheres used in KKR and the MT radius in FP-LAPW. Since in KKR calculations [1] they use the same radius of ASA sphere for the ‘big’ Pt atom and the ‘smaller’ Co atom, this difference can become significant and affect both the charge and spin density distributions.

The XMCD experiments measure not the M_L itself but the M_L per d-hole ratio M_L/n_h . The M_L/n_h calculated in KKR and FP-LAPW for unrelaxed geometry and making use of LSDA is a factor of two smaller than one measured by XMCD. It was already mentioned above that reference [1] proposed the use of the Brooks OP with reduced B_R in order to improve the agreement with experimental data. Here we show that the B_R reduction alone does not solve the problem. Rather it attempts to compensate for limitations of the calculations without taking account of structural relaxation in open systems including an important class of 3d-adatoms and clusters.

Next, we turn to the salient aspect of our investigation, the LSDA + U calculations. When the same Co–Pt interatomic

Table 1. Spin (M_S), orbital (M_L) magnetic moments (in μ_B), and orbital moment per d-band hole (n_h) for a Co atom on Pt(111) resulting from the LSDA and LSDA + U calculations.

Co adatom/Pt(111)	KKR [1]	M_S	M_L	M_L/n_h
LSDA		2.14	0.60	0.25
LSDA+OP/2		2.14	1.50	0.63
CoPt ₁₂	FP-LAPW	M_S	M_L	M_L/n_h
LSDA		2.18	0.57	0.20
LSDA + U	$U_{Co} = 2.0$ eV, $J_{Co} = 0.9$ eV			
Unrelaxed	$d_{Co-Pt} = 4.27$ au	2.23	2.07	0.70
Relaxed	$d_{Co-Pt} = 3.48$ au	2.14	1.58	0.54
Experiment	XMCD [1] $n_h = 2.4$		1.1 ± 0.1	0.46 ± 0.04
Experiment	XMCD ($n_h = 2.92$)		1.34 ± 0.12	

distance as for pure Pt is used, the calculated M_L and M_L/n_h are quite big (see table 1). By varying d_{Co-Pt} and minimizing the total energy we find the equilibrium $d_{Co-Pt} \approx 3.48$ au, i.e. reduced by almost 20%. Since we do not perform a full relaxation and the amount of Pt in our supercell is relatively small, we cannot claim that this will be the correctly optimized d_{Co-Pt} . Nevertheless it is reasonable to assume that the calculated d_{Co-Pt} distance is approximately correct³.

The change in d_{Co-Pt} has a strong effect on M_L and M_L/n_h (shown in table 1). M_L/n_h becomes fairly close to the experimental value and the agreement for M_L is also substantially improved. We should keep in mind that the ‘experimental’ value is given as a product of the measured M_L/n_h ratio times the KKR calculated n_h of 2.4. Making use of the LSDA + U calculated $n_h = 2.9$, we obtain the ‘experimental’ M_L of $1.34 \pm 0.12 \mu_B$, which is in good agreement with the LSDA + U calculated value.

To understand how the enlargement of the Co M_L in the LSDA + U approach comes about we consider the spin and orbitally resolved 3d densities of states (dDOS), which are shown in figure 2. The spin-resolved dDOS (see figure 2(a)) reveals a substantial narrowing of the band width from ~ 6 eV for hcp Co to ~ 4 eV for the Co adatom as well as a moderate increase in the spin-splitting, as is expected for the reduced Co coordination. The spin-down DOS is split at the vicinity of E_F . When dDOS is resolved in terms of cubic harmonics (see figure 2(b)), it becomes clear that the spin-down peak below E_F possesses $e_g: 3z^2 - r^2$ -orbital character while the spin minority d-holes are of $e_g: x^2 - y^2$ and t_{2g} -orbital character.

Since the spin-up Co d-band is fully occupied, only changes of the spin-down band are essential for the M_L enhancement. The m_l -resolved Co dDOS is shown in figure 2(c) for the spin-up and spin-down channels. The major contribution to the increase of M_L originates from $|m_s = -\frac{1}{2}; m_l = +2\rangle$ orbital. The M_L enhancement is brought about by in-plane spin-down $x^2 - y^2$ and xy orbitals and is much less affected by out-of-plane xz, yz orbitals. The spin-down $3z^2 - r^2$ ($\sim |m_l = 0\rangle$) orbital does not contribute to M_L . This out-of-plane $3z^2 - r^2$ orbital is the most localized due to the smallest overlap between Co 3d and Pt 5d electrons.

It is necessary to mention that our analysis cannot be regarded as truly *ab initio* due to the use of external

Coulomb U . Herein we make use of a ‘commonly used’ value of $U = 2$ eV while it can be at least in principle obtained from constrained LSDA calculations [11]. With increase of U the M_L value will increase, and with decrease of U it will decrease. Nevertheless our results show quantitatively the role of the Coulomb U in M_L formation.

Also, we did not consider here the magneto-crystalline anisotropy (MAE) induced by Co adatom. In contrast to M_L , which is mostly a local property of the Co atom, the MAE will consist of contributions from the Co atom as well as the Pt neighbors due to strong Pt atom SOC [8]. Most probably, quantitative studies of the MAE will require a bigger supercell; this is the subject of further work.

Still we can make a rough estimate of the contribution of the Co adatom to the MAE. When spin is rotated from the z -axis (out-of-plane) to the x -axis (in-plane) direction there is only a little change in the value of the Co atom M_S , from $2.14 \mu_B$ (z -axis) to $2.16 \mu_B$ (x -axis). The change in M_L is substantially greater, from $1.58 \mu_B$ (z -axis) to $1.42 \mu_B$ (x -axis). Indeed, this strong anisotropy in M_L paves the way for the strong MAE. Qualitatively, the contribution of the Co atom to the MAE can be estimated by making use of Bruno’s relation [13] $MAE [= (E_x - E_z)] \approx -\xi/4(M_L^x - M_L^z)$, where ξ is the SOC constant (76 meV for a Co adatom). In the LSDA + U calculations, we obtain a MAE of ≈ 3.2 meV/Co which is smaller than the experimental value of 9.3 ± 1.6 meV. A similar estimate for the LSDA calculations yields a MAE of 2.0 meV/Co. While our estimate gives a MAE which is smaller than the experimental data, it is exceptionally large compared with other Co-based materials: a few tenths of a meV for Co/Pt and Co/Au multilayers, and 2.0 meV for Co monatomic wire [14].

We note that the orbital moment enhancement has been recently investigated in [14] for the case of the Co monatomic wire on the Pt(111) surface step edge. Making use of XMCD an experimental value for the Co atom, $M_L = 0.68 \pm 0.05 \mu_B$, was found, which is somewhat smaller than for the Co adatom case. Also, it was shown that LSDA yields the Co monatomic wire $M_L \sim 0.16 \mu_B$ which is substantially smaller than the XMCD experimental value (see e.g. [15]). Using Coulomb U increases the M_L value to $0.45 \mu_B$ [16], substantially improving the agreement with the experimental data.

In conclusion, employing correlated band theory LSDA + U calculations we have provided a microscopic picture of the anomalous enhancement of the Co adatom orbital moment.

³ GGA calculations using scalar-relativistic VASP code for bigger supercells and allowing out-of-plane relaxation for Pt atoms yield d_{Co-Pt} of about 3.1–3.2 au, even smaller than in the present calculations [12].

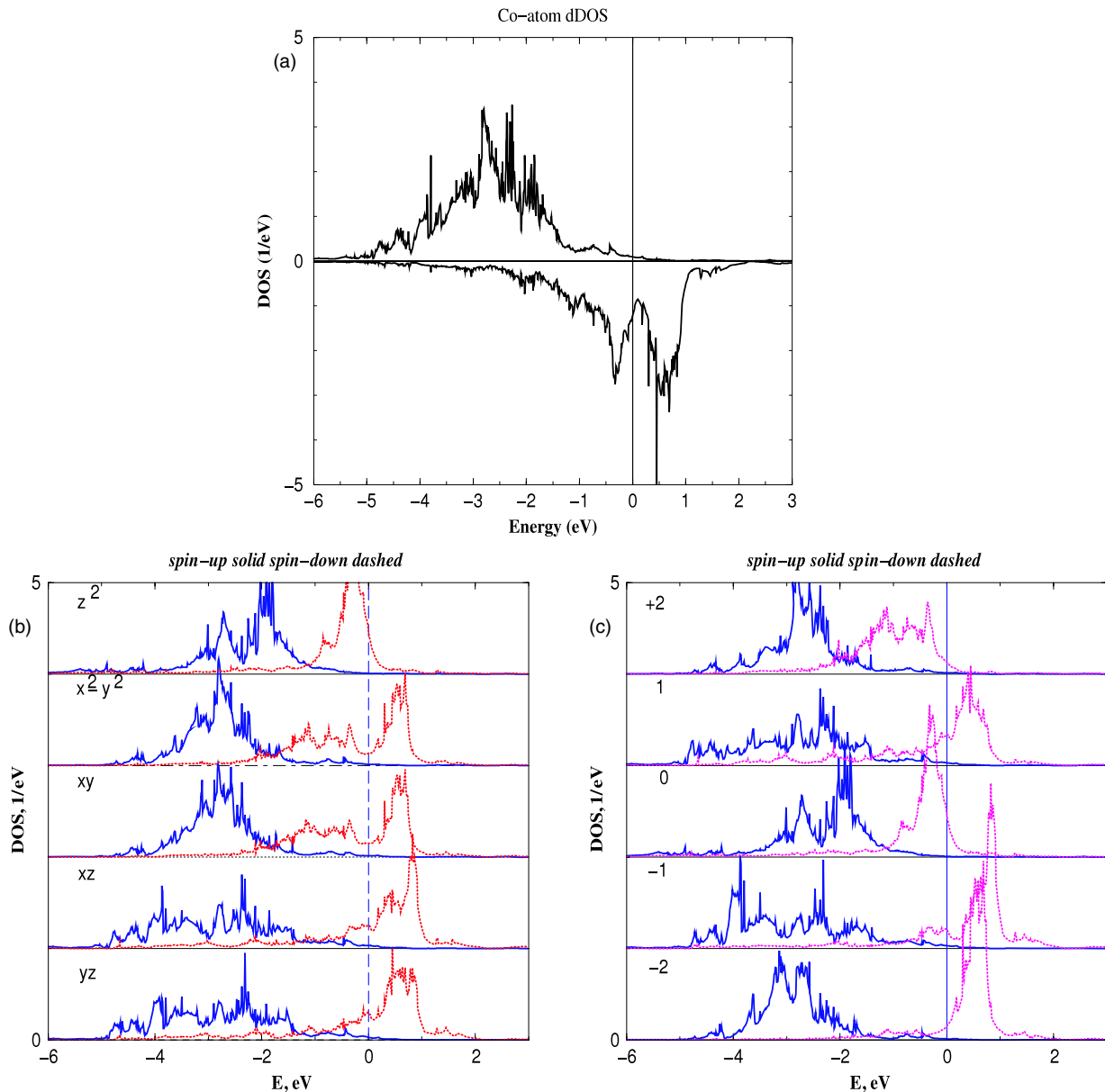


Figure 2. DOS for a Co adatom on Pt(111): (a) spin-resolved Co atom dDOS; (b) Co atom dDOS resolved in cubic harmonics; (c) Co atom dDOS resolved in complex harmonics.

It is found that two major effects need to be included in order to essentially improve the Co orbital moment: (i) a correct LSDA + U orbital polarization due to the Coulomb U and (ii) structural relaxation of the Co–Pt interatomic distance. The calculated value of M_L is found to be in fairly good agreement with experimental XMCD data [1] when those effects are taken into account.

Acknowledgments

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