

Magnetic behavior of $3d$ impurities in Cu, Ag, and Au: First-principles calculations of orbital moments

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We perform first-principles calculations to investigate the behavior of orbital moments (OM's) of $3d$ impurities in Cu, Ag, and Au. Previous calculations for Fe impurities in Ag and Au indicate that in Ag, where the d band is located at lower energies, the Fe impurity has a significant OM, while in Au, where the shallower d band hybridizes strongly with the Fe d levels, the OM is extremely small, practically quenched. One of our objectives here is to determine whether the OM's of other $3d$ impurities in Au are equally suppressed, indicating the importance of hybridization with the shallow d -band of the host Au, or if they can be significantly large. We find that, in spite of the importance of hybridization, the behavior of the OM's of $3d$ impurities in Cu, Ag, and Au is not primarily governed by the position of the d band of the host. For all the hosts considered here, the OM's are negative for early $3d$ impurities and positive for Fe and Co. This behavior, reminiscent of Hund's rule, can be understood in terms of the width and the occupation of the virtual bound states of the up and down bands at the impurity site.

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I. INTRODUCTION

Traditionally it has been assumed that orbital moments (OM's) are quenched in metals and that their influence could be safely neglected when investigating the properties of $3d$ metals and $3d$ sites in metallic systems. While Hund's rule predicts large OM's in the atomic configuration, they seem to be drastically reduced by the presence of crystal fields, and— even more important in $3d$ metallic systems—by hybridization. But there are exceptions to this rule: recent calculations indicate that extremely large orbital moments, in excess of $2\mu_B$, can be present in metals when the hybridization at the site is extremely small, as in the case of some adatoms on Ag(001) surfaces.^{1,2} Furthermore, lately it has been recognized that even relatively small OM's can play a crucial role in the magnetic and hyperfine properties of these systems.³ As an example we stress their relevance to understanding magnetic anisotropy, important for technological applications, which has been demonstrated by a variety of experiments and calculations.⁴ It is now clear that, under appropriate conditions, orbital moments can be of importance in metals, and therefore should be investigated.

That hybridization plays an important role in reducing the orbital moments of $3d$ materials has been clearly demonstrated by time-dependent perturbed angular distribution (TDPAD) studies of Fe in a large number of hosts across the periodic table.⁵ Substitutional Fe replaces a host atom (or enters into a vacancy) and in spite of possible lattice relaxation, usually occupies a space which is roughly determined by the volume per atom of the host.⁶ The experiments show that in most hosts, the Fe impurity exhibits the usual negative hyperfine field, which is characteristic of a situation dominated by spin magnetism. On the other hand, for s - p hosts with very large volumes per atom, the hyperfine field of Fe was found to be positive, indicating that the orbital contribution to the hyperfine fields is probably dominant.⁷ There is actually strong evidence that $3d$ and $4d$ ions implanted into

alkali-metal hosts such as K, Cs, and Rb develop an ionic-type magnetism, with very localized nearly atomic d -shell configurations.^{7,8} A typical case is that of Fe in Cs, for which large positive hyperfine fields have been measured. We note that the Cs host has a very large volume per atom and a valence of 1, yielding a low electron density of the valence electrons. The hybridization between the d electrons of Fe and the Cs host under these conditions is extremely small, resulting in a nearly atomic configuration for the $3d$ electrons of Fe, where large orbital moments and correspondingly high contributions to the hyperfine field are to be expected. Another example of high orbital moments due to these quasiautomatic configurations was recently observed for Fe in Cs in thin films⁹ and confirmed by calculations.¹⁰ Recently very high orbital moments were predicted for some $3d$ and $5d$ adatoms on Ag(001).¹ This can be explained by the small coordination number of the sites, leading to small hybridization and, as a consequence, to extremely narrow, nearly atomic d -band configurations.

Recently Fe impurities in Ag and Au were investigated using a combination of TDPAD measurements and calculations by two different theoretical approaches.³ Fe in Ag and Au are interesting systems because, even though the impurity has similar spin moments in the two hosts, their hyperfine fields differ by about 17 T. It was shown that this difference arises in large part from orbital contributions,³ which are significant for Fe in Ag, but close to zero for Fe in Au. Here we note (see Fig. 1) that the hybridization of the Fe d states in the up band with the deep d band of the Ag host is small, being much stronger in the case of the shallower d bands of the Au host. The high OM of Fe in Ag has been attributed to this smaller hybridization with the host d bands, leading to a greater tendency towards quasiautomatic behavior. On the other hand, the low values of the orbital moment for Fe impurities in Au would be a consequence of the much stronger hybridization between their $3d$ states and the host d band.

Here we use the first-principles real space linear muffin-

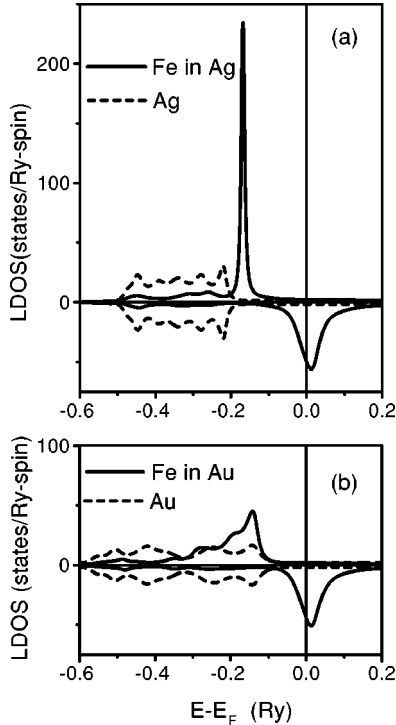


FIG. 1. Local density of states of Fe impurities in (a) Ag and (b) Au hosts. The LDOS of pure (a) Ag and (b) Au are shown in dashed lines for comparison.

tin formalism in the atomic sphere approximation¹¹ (RS-LMTO-ASA) to investigate the magnetic behavior of $3d$ impurities in Cu, Ag, and Au. The method is based on the well-known LMTO procedure^{12,13} and has been applied with success to study crystalline materials, surfaces, multilayers, as well as impurities and defects in these systems.^{11,14} One of the motivations of the present work is to investigate whether a behavior similar to that of Fe in Au, where the orbital moment is extremely small, suggesting quenching, should also be expected for other $3d$ impurities in Au. The problem is especially interesting in view of the nuclear orientation and NMR experiments for Co impurities in Au, which show a very high Knight shift,¹⁵ suggesting that the Co impurity in Au may have rather large orbital moments, in spite of the strong hybridization between the d bands of the impurity and those of the Au host. The paper is organized as follows: in Sec. II, using a simple example, we show how hybridization can contribute to the reduction of the orbital moments. A brief description of the formalism used here is given in Sec. III. In Sec. IV we present and discuss the results. Finally, in Sec. V, we draw our main conclusions.

II. ORBITAL MOMENT AND VIRTUAL BOUND STATES

In textbooks much is said about crystal fields and orbital quenching, but very little about the role of hybridization, probably the dominant effect in the metallic systems considered here. The d bands of $3d$ impurities in simple metals are normally well represented by a virtual bound state,¹⁶ typical of $3d$ levels broadened by hybridization with the surrounding s - p electrons. The local density of d states (LDOS) at the

impurity site is then represented by sharp peaks, characterized by a certain width which depends on hybridization. When totally occupied, these virtual bound states can contain one electron for each m_ℓ and spin.

To illustrate the concept I show in Fig. 1 the LDOS of Fe impurities in Ag [Fig. 1(a)] and in Au [Fig. 1(b)], obtained from first principles calculations using the RS-LMTO-ASA approach.³ The LDOS of the corresponding host [Ag in Fig. 1(a) and Au in Fig. 1(b)] is also shown, as dashed lines, in each of the figures. In both cases, the down bands of Fe, higher in energy, do not interact with the d bands of the host, and have the typical bell-shaped form of a virtual bound state. In Ag, the hybridization of the $3d$ states of the impurity with the $4d$ band of the host, which is deep and appears at lower energies, is very small. Therefore the $3d$ states in the up band of Fe in Ag [see Fig. 1(a)] also exhibit the peak characteristic of virtual bound states, which in the present case, where the hybridization with s - p electrons is also small, is extremely sharp. The $3d$ states in the up band of the Fe impurity in Au, in contrast, hybridize strongly with the shallow $5d$ -band of the host, which is located at similar energies. In this case [see Fig. 1(b)] the LDOS exhibits features and shoulders, losing the bell-shaped form characteristic of a virtual bound state.

It is actually easy to see why the hybridization reduces the orbital moment of d sites in metals and we use a simple example to illustrate this fact. In this example we consider $3d$ -impurities in simple metals and assume that, as discussed above, the LDOS of each of the d levels with orbital quantum numbers $m_\ell = 2, 1, 0, -1, -2$ and spin quantum numbers $m_s = 1/2, -1/2$ is well represented by virtual bound states. To make the arguments more transparent, let us focus our attention on the hypothetical case of a pair of states $m_\ell = 1$ and $m_\ell = -1$ with spin up, $m_s = 1/2$, which are to be occupied by a single electron. We note that, in a cubic system, $3d$ states characterized by the same modulus of m_ℓ ($m_\ell = \pm 1$ or $m_\ell = \pm 2$) should be degenerate, but the degeneracy is broken in the presence of the spin-orbit coupling $\alpha \vec{L} \cdot \vec{S}$. If the wave function is expressed in a basis of spherical harmonics, a diagonal term of the form $\ell_z s_z$ will be present in the Hamiltonian and the center of these previously degenerate bands will be shifted in different directions in energy, depending on the sign of m_ℓ .^{12,17} This splitting will normally be further enhanced if the self-consistent orbital polarization (OP) scheme proposed by Brooks¹⁸ is implemented. For the spin-up states considered in the example, the eigenvalue of s_z will be given by $m_s = 1/2$ and the eigenstate of ℓ_z with $m_\ell = -1$ will have a lower energy than the one associated with $m_\ell = 1$. This is schematically illustrated in Fig. 2, both in the absence (left side) and in the presence (right side) of hybridization. In the absence of hybridization, the d electrons are placed in well-defined, atomiclike, energy levels: a single electron will occupy the level with $m_\ell = -1$, which has the lowest energy. As shown in Fig. 2 (left), the contribution to the orbital moment coming from these energy levels, given by the sum of the product of m_ℓ times the occupation of each level, will be $1 \mu_B$. In Fig. 2 (right), the levels were broadened into bands by the presence of hybridization, and the

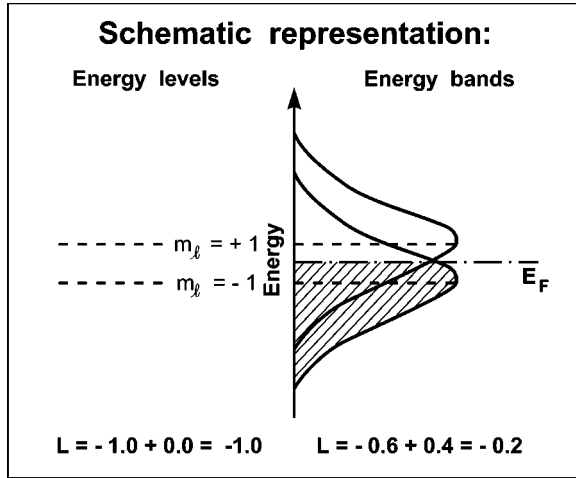


FIG. 2. Schematic representation illustrating the origin of the orbital moment L in the absence (left side) and in the presence (right side) of hybridization.

lowest energy states were filled with a single electron, up to the Fermi level. Now both m_ℓ states have the fractional occupation typical of metals. The contribution to orbital moment coming from these two levels is again given by the sum of the products of m_ℓ times the occupation for each of the levels, here $-0.2\mu_B$, considerably smaller than that of the atomiclike configuration shown in Fig. 2 (left). As the width of the band becomes smaller relative to the splitting between the levels, the orbital moment increases in magnitude, and in the limit of very sharp virtual bound states, it tends to that of the atomiclike configuration. Here, for clarity, the splitting of the levels relative to the bandwidth was slightly exaggerated, leading to differences in occupations of order of 0.2 electrons. In most cases these differences are smaller, yielding correspondingly smaller contributions to the orbital moment.¹⁷ The above arguments can be repeated for unfilled down bands, but there $m_s = -1/2$ and the state with $m_\ell = 1$ will be lower in energy than that with $m_\ell = -1$, and the resulting orbital moment will be positive. The pair of states with quantum numbers $m_\ell = 2$ and $m_\ell = -2$ with spin indices $m_s = 1/2$ and $m_s = -1/2$ behave in a similar way, while the state with $m_\ell = 0$ gives no contribution to the orbital moment. Of course this picture is highly idealized: the bands corresponding to the levels, after being shifted in different directions, may not be rigorously identical and, even in the case of impurities, the shape of the LDOS may differ from the simple form expected for a virtual bound state [cf. the up band of Fig. 1(b)]. But the qualitative behavior is rather well described: as expected from this simple model, unfilled up bands will usually give negative contributions to the LDOS, while the contributions from unfilled down bands will normally be positive.

III. THE RS-LMTO-ASA SCHEME

In this section we give a brief outline of the RS-LMTO-ASA scheme used in our calculations. A detailed description of the method and its application to impurity systems can be found elsewhere.¹¹ The RS-LMTO-ASA is a first-principles,

self-consistent scheme, which follows the steps of the LMTO-ASA formalism, but uses the recursion method¹⁹ to solve the eigenvalue problem directly in real space. As in other first-principles approaches, the exchange and correlation terms are treated within the local spin-density approximation (LSDA). It is a linear method and the solutions are accurate near a given energy E_ν , usually taken at the center of gravity of the occupied bands. We work in the orthogonal representation of the LMTO-ASA formalism, and expand the Hamiltonian in terms of tight-binding (TB) parameters, neglecting terms of order $(E - E_\nu)^3$ and higher. The orthogonal Hamiltonian can then be written as¹³

$$H = E_\nu + \bar{h} - \bar{h}\bar{o}\bar{h}, \quad (1)$$

where

$$\bar{h} = \bar{C} - E_\nu + \bar{\Delta}^{1/2} \bar{S} \bar{\Delta}^{1/2}. \quad (2)$$

Here \bar{h} is a Hermitian matrix; \bar{C} , $\bar{\Delta}$, and \bar{o} are potential parameters of the tight-binding LMTO-ASA representation; and \bar{S} is the structure constant in this same representation. The matrix \bar{S} connecting different sites decays exponentially with increasing intersite distance and \bar{h} has a TB form. To solve the eigenvalue problem in real space we consider a large cluster to simulate the system, and use the recursion method¹⁹ with the Beer-Pettifor terminator²⁰ to complete the recursion chain. We note that the method is rather general, yields onsite and intersite Greens functions, and may be employed to calculate any desired one-electron property.

To evaluate orbital moments we use the scalar-relativistic approach and include the spin-orbit coupling $\alpha\vec{L}\cdot\vec{S}$ self-consistently at each variational step.¹⁷ In the case of 3d metals the results obtained by this approach are generally in very good agreement with those obtained using the spin-polarized Dirac equation.^{3,17} We also present results obtained taking into account OP corrections as suggested by Brooks.^{17,18} In this work, the wave function is expanded in a basis of spherical harmonics and the effect of the Brooks OP term is essentially to shift the center of the up (or down) d band of quantum number m_ℓ by $-BLm_\ell$, where B is the Racah parameter and L the total orbital moment associated with the up (or down) d band at each site in the metal.¹⁷ To obtain the Racah coefficient we have used the expression for the LMTO basis function, in the orthogonal formalism, at the impurity site. Both L_σ and B_σ are recalculated for each spin σ , at each iteration, until self-consistency, for both spin and orbital moments at each site, is achieved.

IV. RESULTS AND DISCUSSION

Here we present results for spin and orbital moments of substitutional V, Cr, Mn, Fe, and Co impurities in Cu, Ag, and Au. The Ni impurity was not included, since preliminary results indicate that it does not develop a magnetic moment in these hosts. The RS-LMTO-ASA calculations were performed using large fcc clusters of ≈ 9000 atoms, with the experimental lattice parameters of the corresponding host. Lattice relaxation around the impurity has been neglected.

TABLE I. Results (in μ_B) for the orbital moments of V, Cr, Mn, Fe, and Co impurities in Cu, Ag, and Au hosts. Values obtained with (Yes) and without (No) the inclusion of orbital polarization (OP) are shown in each case.

Host	OP	V	Cr	Mn	Fe	Co
Cu	No	-0.023	-0.029	0.005	0.092	0.109
	Yes	-0.039	-0.037	0.008	0.206	0.274
Ag	No	-0.050	-0.037	-0.005	0.134	0.267
	Yes	-0.096	-0.041	-0.005	0.680	1.40
Au	No	-0.052	-0.069	-0.033	0.008	0.228
	Yes	-0.095	-0.083	-0.034	0.067	1.11

This is a good approximation when the volume per atom of the impurity in the metal is comparable to or smaller than that of the host. Except for V and Cr impurities in Cu, this condition is always satisfied here. We have considered a basis with nine orbitals (corresponding to s , p , and d electrons) per site, for each spin. Since the spin-orbit term mixes spin-up and spin-down electrons, the matrices connecting the sites have dimension 18×18 . The eigenvalue problem was solved in real space by taking 20 levels of recursion and using the Beer-Pettifor terminator²⁰ to complete the chain. The RS-LMTO-ASA calculations are performed within the LSDA and here the exchange and correlation potential of von Barth and Hedin²¹ was used. We have taken \bar{h} to connect both first and second neighbors in the fcc structure, but since the structure constant decays exponentially with distance, the interaction with second neighbors is already very small. We note that in the last term of Eq. (1) \bar{h} is applied twice, therefore the Hamiltonian H is more extended, connecting up to second neighbors of second neighbors.

The calculations were performed in two ways: with and without the inclusion of OP. The spin moment is practically the same in the two cases, but the orbital moment is significantly enhanced when OP is included. This is seen from Table I, where results for the orbital moment with (OP) and without (No OP) orbital polarization are shown. In the case of the OP results I also show, in Table II, the separate d -spin-up and d -spin-down contributions to the orbital moment. To the best of my knowledge, no systematic study of the behavior of the orbital moments in Cu, Ag, and Au is available. But in the case of Fe and Co impurities in Ag some isolated values, obtained using the Korringa-Kohn-Rostoker (KKR) formalism² and the LMTO approach in a supercell,^{10,22} are given in the literature. Our OP result of $0.68\mu_B$ for the orbital moment of Fe in Ag is in good agreement with the values of $0.60\mu_B$,²² $0.68\mu_B$,¹⁰ and $0.80\mu_B$ (Ref. 2) given in the literature. For Co impurities in Ag, the OP results show a similar tendency, but the discrepancies are larger. We find an orbital moment of $1.4\mu_B$, while the full potential LMTO approach gives $1.5\mu_B$ (Ref. 22) and KKR calculations yield $1.7\mu_B$.² In the absence of OP, the magnitude of the OM's is much smaller and all approaches yield similar values. We note that discrepancies in the quantitative values of orbital moments are not uncommon in the literature, as evidenced by the recent calculations for Fe, Co,

TABLE II. Calculated orbital moments (in μ_B) for V, Cr, Mn, Fe, and Co impurities in Cu, Ag, and Au hosts, including orbital polarization (OP). The separate contributions of up (d -up) and down (d -dw) d -bands at the impurity sites are also shown in each case.

Host	Band	V	Cr	Mn	Fe	Co
Cu	d -up	-0.055	-0.044	-0.012	-0.011	0.032
	d -dw	0.016	0.008	0.021	0.217	0.306
	Total	-0.039	-0.037	0.008	0.206	0.274
Ag	d -up	-0.096	-0.041	-0.007	-0.008	0.015
	d -dw	-0.000	0.000	0.003	0.688	1.42
	Total	-0.096	-0.041	-0.005	0.680	1.40
Au	d -up	-0.095	-0.088	-0.020	-0.018	-0.034
	d -dw	-0.000	0.006	-0.014	0.085	1.15
	Total	-0.095	-0.082	-0.034	0.067	1.11

and Ni adatoms on Ag(001), published by different groups using different approaches within the KKR formalism.^{1,23}

In Fig. 3, to better visualize the trends, I plot the results for spin [Fig. 3(a)] and orbital [Fig. 3(b)] contributions to the magnetic moments of $3d$ impurities in Cu (triangles), Ag (squares), and Au (circles) hosts, in the presence of OP. As is usually the case, the spin moments were not affected by the inclusion of orbital polarization and are practically the same with and without OP. The spin moments of $3d$ impurities in Ag and Au are close in magnitude, since both hosts have a similar "size," as measured by their Wigner-Seitz (WS) radii. As expected, moments are lower in Cu, which has a smaller WS radius, leading to a larger hybridization between the $3d$ levels of the impurity and the host. It is clear from Fig. 3(b) that, for all the hosts considered here, the early transition-metal impurities (here V and Cr) have a negative orbital moment (antiparallel to the spin moment), while the late ones (here Fe and Co), have positive ones. The sign of the orbital moment changes around Mn, which has an orbital moment close to zero and, depending on the host, can be either positive or negative. This behavior is a remnant of Hund's rule, in the sense that it also predicts antiparallel alignment between orbital and spin moments in early transition metals and parallel alignment for late transition metals.

The trends obeyed by the orbital moments of $3d$ impurities in Cu, Ag, and Au can be qualitatively understood in terms of virtual bound states if we remember that, due to the diagonal term in $L \cdot S$, the center of the bands with negative m_ℓ tends to lie lower in energy in the case of up bands, leading to a higher occupation of virtual bound states with negative m_ℓ and therefore to negative contributions to the orbital moment. The opposite is true for down bands, where contributions to the orbital moment tend to be positive. Even though some exceptions are found when the moments have small magnitudes, this is in general confirmed by the signs of calculated d -up and d -down contributions of Table II. One expects that the shifts in the centers of the d bands associated with different quantum numbers m_ℓ will lead to greater charge redistribution among the bands, and therefore higher contributions to the orbital moment, when the density of states at the Fermi level is high. Remembering that the up

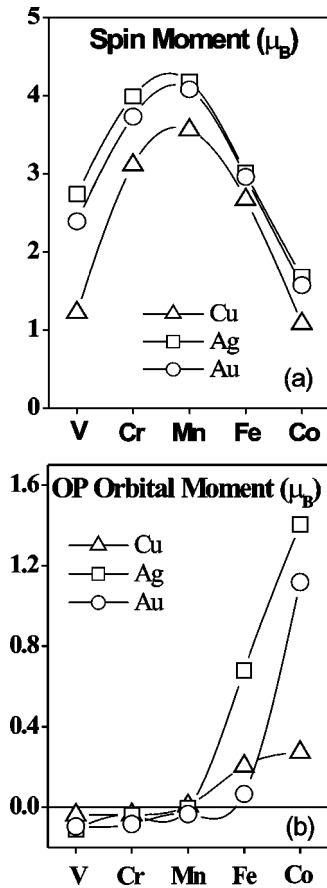


FIG. 3. Calculated (a) spin and (b) orbital contributions to the magnetic moment of 3d impurities in Cu, Ag, and Au hosts. Orbital polarization (OP) has been included.

band leads to positive contributions and the down band to negative, the magnitude of the orbital moment should be roughly proportional to the difference in LDOS at the Fermi level between the down and the up band. This rule has actually been suggested by Ebert²⁵ as a means of estimating the magnitude of the orbital moment, and it works quite well.

In the case of a virtual bound state, the density of states at the Fermi level is governed by two factors: the hybridization, which regulates the bandwidth, and the occupation. The up or down LDOS at the Fermi level will be high if the virtual bound state associated with the corresponding d level is sharp (low hybridization with the host) and the band is close to half occupied (around 2.5 electrons), placing the Fermi level near the maximum of the virtual bound state peak. Very high and very low band occupations lead to low values of the density of states at the Fermi level, and low contributions to the orbital moment. Regarding the bandwidth, one can say that in general the virtual bound states of 3d impurities in Ag and Au are expected to be sharper than those of impurities in Cu, for which a stronger hybridization between the impurity levels and the host is present. Also, because their 3d levels are more extended, the bandwidths of the virtual bound states are usually larger for V and Cr impurities than for Fe and Co impurities, which tend to exhibit sharper bound states. In Table III, calculated values for the up (d -up) and down (d -dw) d occupations of 3d impurities in Cu, Ag, and

TABLE III. Calculated d occupations for up and down bands of 3d impurities in Cu, Ag, and Au. Bands close to half filled, having between 1.5 and 3.5 electrons, have their occupations highlighted in bold face numbers.

Host	Band	V	Cr	Mn	Fe	Co
Cu	d -up	2.18	3.72	4.45	4.57	4.38
	d -dw	1.22	0.74	0.98	1.94	3.27
Ag	d -up	3.09	4.23	4.75	4.77	4.71
	d -dw	0.45	0.36	0.70	1.83	3.08
Au	d -up	2.90	4.11	4.75	4.78	4.69
	d -dw	0.65	0.50	0.75	1.83	3.11

Au in the presence of OP are given. Bands close to half full (occupations between 1.5 and 2.5 electrons) are highlighted, by showing their occupation numbers in boldface. If one compares the up and down contributions to the orbital moment in Table II with the corresponding occupations given in Table III, a clear correlation is seen: very high (between 3.5 and 5) and very low (between 0 and 1.5) band occupations lead to low values of the density of states at the Fermi level, and low contributions to the orbital moment, while for occupations between 1.5 and 3.5 (boldface in Table III) the value of the orbital moments tends to be significant. The early transition metals like V tend to have a partially occupied up band (the contribution to the orbital moment is large and negative) and a down band which is almost empty (with negligible contributions), resulting in a negative value of orbital moment. For Cr and Mn sites with strong spin moments, the up band tends to be almost full, while the down band tends to be almost empty, yielding the small orbital moments calculated for these sites. Finally, in the case of Fe and Co, the up band is almost full, giving small contribution, while the down band is partially filled, yielding large positive contributions to the orbital moments.

We note that even though trends are well explained by this simple virtual bound state model, deviations can occur, mainly for two reasons: (i) the rigid band approach, which assumes that the LDOS is just shifted in energy while keeping the same shape, is oversimplified; (ii) as was seen for the up band of Fe in Au [Fig. 1(b)], hybridization with the d bands of the host can significantly change the shape of the LDOS from a clear-cut peak, observed in simple metals, to a more complicated structure with valleys, shoulders, etc. These deviations can determine the quantitative behavior of the orbital moment, including the point along the d series at which the orbital moment changes from positive to negative in the different hosts. This should be kept in mind when analyzing the results.

Now we address the question of the low orbital moment of Fe in Au, when compared to that of Fe in Ag. The results indicate that hybridization with the 5d band of the host, even though important, is not the main reason for the quenching of the orbital moment of Fe impurities in Au. This is clearly seen by analyzing the LDOS shown in Fig. 1 in conjunction with the values of up and down contributions to the orbital moment shown in Table II. The orbital moments for Fe impurities (see Table II) are strongly dominated by the down

spin contributions. But it is clear from Fig. 1 that the down states, being higher in energy, are not significantly affected by hybridization with the d states of the host, which under these conditions cannot be directly responsible for the low orbital moment of Fe in Au. The low orbital moment obtained for Fe in Au is simply due to the fact that, when going from negative to positive values across the $3d$ series, the orbital moment in Au seems to pass through zero closer to Fe, while for Ag the crossing is earlier, near Mn. We should note that the position where the orbital moment crosses from positive to negative along the $3d$ series depends on the details of hybridization with the host, and in this sense, the hybridization with the host d bands do in this indirect way influence the results.

It is clear from the above results that the orbital moments of $3d$ impurities in Au are not, in general, quenched by hybridization with the shallow d band of the host. The trends obeyed by the orbital moments are actually similar in Ag and Au, as can be seen from Fig. 3. In the case of Co in Au, a large calculated orbital moment (of around $1.1\mu_B$) was obtained in the presence of OP, yielding an orbital to spin moment ratio of 0.7. A lower, but still surprisingly high, orbital to spin ratio of about 0.34 has been recently observed experimentally for Co in Au using the x-ray magnetic circular dichroism (XMCD) technique, evidencing beyond any doubt that the moment of $3d$ impurities in Au is not, in general, quenched.²⁴ This measured value of the orbital to spin ratio is much larger than the one calculated in the absence of OP, and supports the notion that the inclusion of OP is necessary to explain the experimental data, but that it tends to overestimate the magnitude of the orbital moment. We note that recently a 50% reduced Racah parameter has been used in OP calculations, to reduce OP orbital moments, and better describe the experimental behavior of Co atoms and nanoparticles in Pt(111).²⁶ In this context we should comment on the recent TDPAD experiments determining the hyperfine field,³ which point to an orbital moment of the order of $0.35\mu_B$ for Fe in Ag, and to small orbital moments, close to zero, for Fe in Au. For Fe in Au, the calculated orbital moments are also small, in good agreement with experiment. But for Fe in Ag, the present calculations give values of $0.13\mu_B$ and $0.68\mu_B$ for the orbital moment, with and without orbital polarization, respectively, and again the experimental value is better represented if an average between the values with and without OP is taken.

V. CONCLUSIONS

In this work, we have used the RS-LMTO-ASA formalism to investigate the OM's of $3d$ impurities in Cu, Ag, and Au. The orbital moment was obtained both with and without inclusion of orbital polarization, which when included sig-

nificantly increases its magnitude. The spin moments of $3d$ impurities were found to be similar in Ag and Au but lower in Cu, where due to the smaller size of the host, the hybridization is stronger. The orbital moments show similar trends in all three hosts, being negative for early transition metals and positive for Fe and Co in all hosts. This behavior can be understood in terms of a simple model based on virtual bound states.

Our results show that the orbital moments of $3d$ impurities in Au are not, in general, quenched by hybridization with the shallow $5d$ band of the host. This is in accordance with nuclear orientation and NMR measurements which suggest that Co in Au should exhibit a significant orbital moment.¹⁵ In our calculations, a very large orbital moment and a correspondingly large orbital to spin moment ratio is obtained for Co in Au, both with and without inclusion of orbital polarization. Recent XMCD measurements point to an experimental ratio lying between these two values. Orbital moments inferred from TDPAD measurements of the hyperfine field of Fe in Ag are also better represented by an average between calculated values with and without the inclusion of OP, again suggesting that the inclusion of OP is necessary to explain orbital moments, but tends to overestimate their magnitudes.

Finally, we find that the behavior of the orbital moment of $3d$ impurities in Cu, Ag, and Au contains a remnant of Hund's rule, in the sense that it also predicts antiparallel alignment between orbital and spin moments in early transition metals and parallel alignment for late transition metals. Recent XMCD measurements for $3d$ impurities in Au confirm these trends.²⁴ A similar behavior was also found for orbital moments of $3d$ adatoms in Ag(001), where the d levels are also broadened into virtual bound states.¹ There, due to the incomplete coordination of adatoms, the hybridization with the host is smaller, leading to very sharp virtual bound states and large magnitudes for orbital moments, which can be, in some cases, close to those given by Hund's rules in the corresponding atoms.

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