Orbital magnetic moment and extrinsic spin Hall effect for iron impurity in gold

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We report electronic structure calculations of an iron impurity in gold host. The spin, orbital and dipole magnetic moments were investigated using the LDA+U correlated band theory. We show that the around-mean-field-LDA+U reproduces the XMCD experimental data well and does not lead to formation of a large orbital moment on the Fe atom. Furthermore, exact diagonalization of the multi-orbital Anderson impurity model with the full Coulomb interaction matrix and the spin-orbit coupling is performed in order to estimate the spin Hall angle. The obtained value $\gamma_S \approx 0.025$ suggests that there is no giant extrinsic spin Hall effect due to scattering on iron impurities in gold.

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During the last several years, a broad interest and attention have been devoted to the spin Hall effect (SHE) in semiconductors [1] and metals [2]. This effect amounts to an observation of a transversal spin current when a charge current is flowing through a solid. The SHE is caused by the spin-orbit coupling (SOC) and can occur even in non-magnetic solids [2].

Recently, an experimental observation of a giant SHE in Au/FePt has been reported [3]. The spin Hall conductivity of $\sim 10^5 \Omega^{-1}\text{cm}^{-1}$ and the spin Hall angle as large as $\sim 0.1$ were measured [3]. Guo et al. suggested the effect to be of extrinsic origin due to the Fe and Pt impurities in gold [4]. They reported local (spin) density approximation (LSDA) plus Coulomb $U$ (LDA+U) solution for Fe in Au with a very large orbital magnetic moment $M_L \sim 1.5 \mu_B$.

The results of Ref. [4] contradict the LDA+U calculations presented in Ref. [3] that reported a tiny $M_L \sim 0.02 \mu_B$. The value of $M_L$ from Ref. [4] is clearly inconsistent with the experimental x-ray magnetic circular dichroism (XMCD) data for the ratio of $M_L$ and the effective spin moment $M_S$, $R_{LS} = 0.634$ [6]. Assuming $M_S \sim 3 \mu_B$ leads to $M_L \sim 0.1 \mu_B$ which is of an order of magnitude smaller than the prediction of Ref. [4]. It was suggested [7] that the discrepancy between Refs. [4] and [3] are due to different choices of the Coulomb $U$. A large value of $M_L$ is calculated with $U = 5 \text{ eV}$ [4], while much smaller ones are obtained with $U = 3 \text{ eV}$ [5].

In this work we revisit the electronic and magnetic structure of the Fe impurity in Au. We examine different flavors of the rotationally-invariant LDA+U method [8]: the “fully localized limit” (FLL) as well as the “around mean field” (AMF) version. The results for the orbital magnetic moment $M_L$ are compared with the available experimental data.

Both LSDA and LDA+U methods yield broken-symmetry static mean-field solutions with ordered spin and orbital moments, whereas the true dynamical solution of an impurity in a non-magnetic host exhibits $M_S = 2\langle \hat{S}_z \rangle = 0$ and $M_L = \langle \hat{L}_z \rangle = 0$ when no external magnetic field is applied and no preferential direction for the orientation of the moments exists. In order to go beyond the static mean-field and to incorporate the dynamical electron correlations, we employ the exact diagonalization (ED) method to solve a multi-orbital single impurity Anderson model (SIAM) [9] whose parameters are extracted from LDA calculations. We evaluate the spectral density at the Fe impurity in Au and estimate the spin Hall angle due to skew scattering on the impurity. A relation between the electronic structure and the extrinsic SHE is discussed.

As a computational model we use a FeAu15 supercell chosen to keep Fe and its 12 nearest Au neighbors separated from other impurity atoms. No relaxation is performed as it is not essential for the closed packed fcc structure. We use the lattice constant of elemental Au, $a = 7.71$ a.u. All calculations are performed making use of a relativistic version (with SOC) of LDA+U implemented in the linearized augmented plane wave (FP-LAPW) basis [10]. The radii of the atomic muffin-tin (MT) spheres are set to 2.3 a.u. (Fe) and 2.5 a.u. (Au). The parameter $R \times K_{\text{max}} = 7.6$ determined the basis set size and the Brillouin zone was sampled with 343 $k$ points. We checked that a finer sampling with 729 $k$ points does not modify the results.

First, we apply the conventional LSDA with the von Barth and Hedin [11] exchange-correlation potential implemented within the relativistic FP-LAPW method [12]. Our results for the spin and orbital moments inside the Fe MT sphere, $M_S$ and $M_L$, are compared with the results of other calculations in Table [1]. In spite of a relatively small (16 atoms only) and unrelaxed supercell, present results are in a fair agreement with VASP [5] results for a substantially larger and relaxed supercell containing 108 atoms, with the tight-binding LMTO (TB-LMTO) results for 55 atom supercell [13], and with the KKR-ASA calculations [14]. All calculations indicate a small value of $M_L$ for Fe impurity in Au, which is typical for 3d
transitional metals and alloys. The calculated $M_L/M_S$ ratio is substantially smaller than the experimental value $R_{LS} = 0.034$ [6]. Typically, $M_L$ is underestimated in LSDA due to the lack of orbital polarization. This leads to a smaller ratio $M_L/M_S$ and explains the disagreement with experiment.

### Table I. LSDA magnetic moments on Fe in Au (in units of $\mu_B$)

|         | $M_S$ | $M_L$ | $M_L/M_S$ |
|---------|-------|-------|-----------|
| FP-LAPW| 3.04  | 0.024 | 0.008     |
| VASP   | 3.08  | 0.040 | 0.012     |
| TB-LMTO| 2.95  | 0.008 | 0.003     |
| KKR-ASA| –     | –     | 0.007     |

![Figure 1](image_url) (Color online) The spin-resolved $d$-orbital DOS for Fe impurity in Au calculated with LSDA (top) and AMF-LDA+$U$, $U = 3$ eV (bottom). Also shown are $e_g$ and $t_{2g}$-like projected DOS for Fe.

The calculated $d$-orbital density of states (DOS) for Fe atom and the first nearest neighbor Au atoms are shown in Fig. 1 (top). LSDA yields fully occupied Fe spin-$\uparrow$ states that are hybridized with shallow Au $d$ states. The Fe spin-$\downarrow$ states are substantially more localized. Analysis of the projected DOS shows that the $e_g$-like ($d_{x^2-y^2} + d_{3z^2-r^2}$) states become practically fully spin-polarized while the $t_{2g}$-like ($d_{xy} + d_{xz} + d_{yz}$) states are only partially polarized, see Fig. 1 (top).

Now we turn to the LDA+$U$ calculations. We compare FLL and AMF variants of the rotationally-invariant LDA+$U$ method. The full local occupation matrix with all spin off-diagonal components is preserved. The double counting of the non-spherical $d$-states contributions to the LSDA and the LDA+$U$ parts of the potential is corrected. The exchange $J = 0.9$ eV was used for Fe (Slater integrals $F_2 = 7.75$ eV, $F_4 = 4.85$ eV). The Coulomb $U$ was varied from 3 eV to 5 eV.

The spin $M_S$, orbital $M_L$ and dipole $M_D$ [15] 3$d$ magnetic moments are given in Table I together with the occupation of the Fe atom $d$ orbitals, $n_d$. Both FLL and AMF flavors of LDA+$U$ lead to an enhancement of $M_L$ with respect to the LSDA estimate. It is due to non-spherical Coulomb and exchange interactions which are incorporated in LDA+$U$ [16] and cause an additional orbital polarization to that induced by the spin-orbit coupling. The value of $M_L$ increases with increase of the Coulomb $U$. It is observed that the FLL double counting yields a substantially stronger enhancement of $M_L$ than the AMF method.

There is also a substantial magnetic dipole moment $M_D$ formed on the Fe impurity. When the spin-orbit coupling is included and spin polarization is allowed, the initial cubic symmetry is broken and only the tetragonal symmetry remains. This effect is rather small in LSDA. It becomes substantially enhanced in LDA+$U$ due to the additional orbital polarization. This effect is visible on the AMF-LDA+$U$ DOS shown in Fig. 1 (bottom). The main difference between LSDA and LDA+$U$ occurs in the spin-$\downarrow$ channel for the $t_{2g}$-like states; the $d_{xy}$ state peels off from the $d_{xz}$ and $d_{yz}$ states and becomes occupied.

Experimental XMCD data are available for Fe impurity in Au [6]. The measured value for $R_{LS} = M_L/[M_S + 7M_D] = 0.034$ is in a very good agreement with our AMF-LDA+$U$ results for $U$ in the range between 3 eV and 4 eV. On the basis of these calculations we conclude that a reasonable value of the Coulomb $U$ for Fe impurity in Au host is $\approx 3$ eV.

Our FLL results for $U = 5$ eV are fairly close to those of Ref. [4] where the LDA+$U$ double counting was not specified. In this case, the calculated $R_{LS} = 0.21$ exceeds the experimental XMCD value by almost an order of magnitude. Therefore, the FLL-LDA+$U$ method does not satisfactorily describe the electronic structure of Fe impurity in Au.

Both the LSDA and LDA+$U$ methods yield broken-symmetry mean-field solutions with non-zero $M_S$ and $M_L$. This is because the part of the Coulomb interaction treated in the Hartree–Fock-like approximation is trans-
TABLE II. Magnetic moments (in $\mu_B$) and 3d occupation $n_d$ of the Fe impurity in Au host as a function of Coulomb $U$.

|      | FLL | AMF |
|------|-----|-----|
| $U$ (eV) | 3   | 4   | 5   | 3   |
| $M_S$     | 3.18| 3.21| 3.29| 2.94| 2.90|
| $M_L$     | 1.24| 1.36| 1.44| 0.16| 0.22|
| $T_{MF}$  | 2.36| 2.71| 3.57| 2.16| 2.35|
| $R_{LS}$  | 0.23| 0.23| 0.21| 0.03| 0.04|
| $n_d$     | 6.00| 6.00| 5.97| 6.03| 6.03|

formed into the exchange splitting field. This exchange field is of the order of a few eV (see Fig. 1) and by far exceeds any imaginable external magnetic field. Thus, the LDA+U method, most probably, provides a reasonable description of the local-moment systems in (strong) external magnetic fields.

When no external magnetic field is applied and no preferential direction for the orientation of the moments exists, neither LSDA nor LDA+U suffice. Recently, an attempt has been made to go beyond the static mean-field approximation and to solve the SIAM for the Fe impurity in Au employing the Hirsch–Fye quantum Monte Carlo method [7]. The authors used a simplified three-orbital model with a diagonal Coulomb vertex and a spin-diagonal spin-orbit coupling only. These simplifications make an estimate of the accuracy of the quantitative results reported in Ref. [7] difficult.

In order to deal with the electronic structure of the Fe impurity in the absence of the external magnetic field, we apply the finite-temperature ED method [17] to the complete five-orbital $d$ shell subject to the full spherically symmetric Coulomb interaction, spin-orbit coupling and a cubic crystal field. The effective multi-orbital impurity Hamiltonian can be written as [9]

$$H - \mu N = \sum_{k \sigma} \epsilon_k b^\dagger_{k \sigma} b_{k \sigma} + \sum_{m \sigma} \epsilon_m d^\dagger_{m \sigma} d_{m \sigma}$$

$$+ \sum_{m' \sigma} \left( (\mathbf{k} \cdot \mathbf{s} + \Delta_{CF})_{m \sigma, m' \sigma} d^\dagger_{m \sigma} d_{m' \sigma} ight)$$

$$+ \sum_{m \sigma} \left( V_k d^\dagger_{m \sigma} b_{k \sigma} + \text{h.c.} \right)$$

$$+ \frac{1}{2} \sum_{m \sigma, m' \sigma} U_{m m', m' \sigma, m \sigma} d^\dagger_{m \sigma} d_{m' \sigma} d_{m \sigma} d_{m' \sigma},$$

where $d^\dagger_{m \sigma}$ creates an electron in the $d$ shell and $b^\dagger_{k \sigma}$ creates an electron in the “bath” which models those host-band states that hybridize with the impurity $d$ shell. The bath is predominantly composed of $s$ and $p$ bands of Au. The impurity-level position $\epsilon_d$ and the bath energies $\epsilon_k$ are measured from the chemical potential $\mu$. Parameters $\xi$ and $\Delta_{CF}$ specify the strength of the spin-orbit coupling and the size of the cubic crystal field on the impurity. They are determined from LDA calculations as $\xi = 60$ meV and $\Delta_{CF} = 32$ meV. The hybridization parameters $V_k$ and the bath energies $\epsilon_k$ do not depend on $m$ and $\sigma$, and thus the Hamiltonian preserves orbital and spin angular momenta. This is a good approximation for Fe in Au, since the lower-symmetry components of the hybridization turn out to be considerably smaller than $\xi$ and $\Delta_{CF}$.

For the ED method to be applicable, the continuum of the bath states is discretized. The parameters $\epsilon_d$, $\epsilon_k$ and $V_k$ are chosen so that the impurity Green’s function corresponding to the discretized Eq. (1) with $U = 0$ approximates the impurity Green’s function from the LDA as closely as possible. Namely, we require several lowest moments of the respective densities of states to coincide, $M_n^{(SIAM)} = M_n^{(LDA)}$, where $M_n = \int \epsilon^g g_n^0(\epsilon)d\epsilon/\int g_n^0(\epsilon)d\epsilon$ [18]. The integrals run over a 1 eV wide interval centered at the Fermi level, which confines the LDA impurity resonance. The actual values of the bath parameters are $\epsilon_k^{(I)} = 80$ meV and $V_k^{(I)} = 220$ meV when the index $k$ is restricted to a single value and the bath contains 10 spinorbitals (bath I: “$d+10$ spinorbitals”). For a bath twice as large we get $\epsilon_k^{(II)} \in \{-310, 340\}$ meV and $V_k^{(II)} \in \{140, 170\}$ meV (bath II: “$d+20$ spinorbitals”). The position of the impurity level $\epsilon_d$ obtained from this procedure is subsequently shifted by a Hartree-like contribution in order to maintain the LDA impurity occupation $n_d = 6.18$ when the local Coulomb term is introduced.

FIG. 2. (Color online) $d$-electron spectral function of the impurity model of Eq. (1) with $U = 3$ eV and two variants of discrete bath: 10 bath spinorbitals (top) and 20 bath spinorbitals (bottom).

After the parameters of the discrete impurity model are set, the band Lanczos method [19, 20] is utilized.
to determine the lowest lying eigenstates of the many-body Hamiltonian and to calculate one-particle Green’s function $G^d_{\text{SIAM}}$. The resulting $d$-orbital spectral function $\text{Im}(G^d_{\text{SIAM}})/\pi$ is shown in Fig. 2 for the two models of the bath and for the Coulomb interaction parameters $U = F_0 = 3$ eV and $J = 0.9$ eV ($F_2 = 7.75$ eV, $F_4 = 4.85$ eV). The inverse temperature $\beta = 500$ eV$^{-1}$ was used in these calculations. Although the details of the spectral peaks depend somewhat on the particular choice of the bath, the overall structure of the spectrum with peak(s) in the vicinity of the Fermi level is preserved when the bath parameters are varied. The spin $S = 1.91$, orbital $L = 2.21$ and total $J = 3.87$ moments are calculated for the $d$ shell from the expectation values $\langle X^2 \rangle = X(X+1)$, $X = S, L, J$. Individual components of the moments, $\langle \hat{S}_z \rangle$ and $\langle \hat{L}_z \rangle$, vanish so that the spin-orbital symmetry is preserved and neither spin nor orbital polarization is induced in the absence of the external magnetic field.

Following Refs. [4, 21], we evaluate the spin Hall angle as a function of the skew scattering on the impurity with a local magnetic moment. For a fixed value of $U$, the Hall angle decreases with increasing hybridization $V$ since the spin-orbit splitting in the host band is negligible and the hybridization thus effectively reduces the spin-orbit effects in the Fe $d$ shell.

Our results are consistent with the measurements of Fert et al. [22] of the anomalous Hall coefficient $\sim 0.01$ in dilute 3$d$ noble metal alloys. The angle $\gamma_S \approx 0.025$ we obtain is 50% smaller than the earlier theoretical estimate $\gamma_S = 0.055$ by Gu et al. [7] and substantially smaller than the “giant” $\gamma_S = 0.11$ reported by Seki et al. [3]. Note that the giant SHE interpretation of the experimental results in Ref. [3] has been recently challenged also from the experimental viewpoint [23].

| Model   | $U$ (eV) | $n_{d}$ | $n_{3/2}$ | $n_{5/2}$ | $\gamma_S$  |
|---------|----------|--------|-----------|-----------|-------------|
| LDA     | 6.18     | 2.62   | 3.55      | 0.008     |
| bath I  | 6.18     | 2.68   | 3.50      | 0.011     |
| bath II | 6.18     | 2.85   | 3.33      | 0.021     |
| bath II | 6.18     | 2.94   | 3.24      | 0.026     |
| no bath | 6.18     | 2.98   | 3.19      | 0.029     |

To summarize, our calculations show that the AMF-LDA+$U$ method with the Coulomb $U$ around 3 eV reproduces very well the XMCD experimental data for Fe impurity in Au host. The calculated orbital moment at the Fe atom, $M_L = 0.16\mu_B$, is almost ten times smaller than that reported by Guo et al. [4]. We explicitly show that the reason for this difference is not only in the use of a smaller value of $U$ [7], but also in the appropriate choice of the LDA+$U$ flavor. Furthermore, using the exact diagonalization of a multi-orbital impurity model, we estimate the spin Hall angle due to the scattering on the Fe impurity in the Au host as $\gamma_S \approx 0.025$. It is substantially smaller than $\gamma_S = 0.11$ reported by Seki et al. [3]. We conclude that scattering off Fe impurities in Au does not yield a giant SHE.

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