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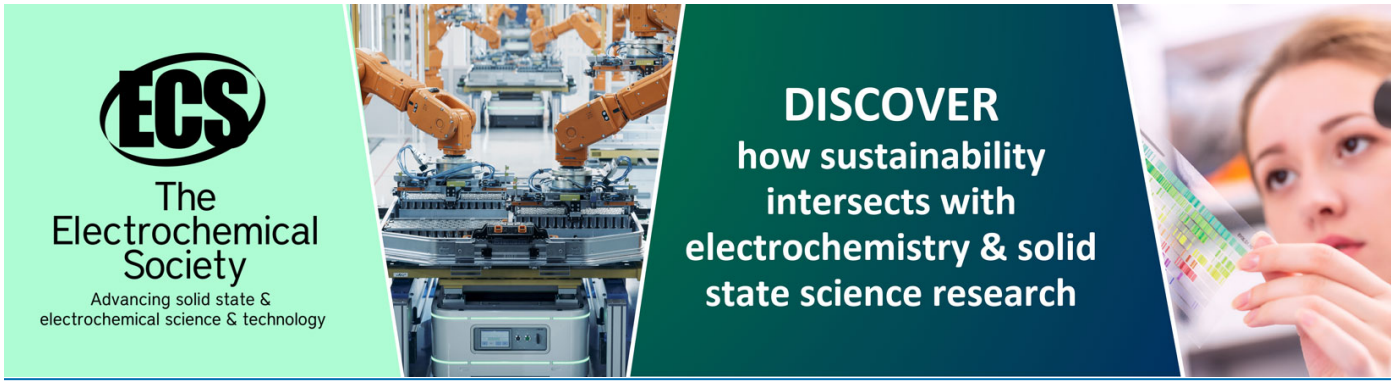

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Orbital-dependent Kondo effect for Fe in Au : Combined approach of density functional theory and quantum Monte Carlo method

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Abstract. We have studied the orbital-dependent Kondo effect for an Fe impurity in Au host by a combined approach of density functional theory and quantum Monte Carlo method. Our results show that the Kondo temperature of e_g electrons is much lower than that of t_{2g} electrons of Fe atoms, and thus support the previous viewpoint of Guo, Maekawa, and Nagaosa [Phys. Rev. Lett. **102**, 036401 (2009)]. In addition, it is found that the difference of impurity-host hybridization is more important than the difference of impurity energy levels to induce the orbital-dependent Kondo effect.

The research for the system of Fe impurities in Au has a long history. It has low Kondo temperature around 0.4K [1], high electric resistance at room temperature [2], and anomalous Hall effect with Hall angle of the order of 0.01 [3]. Recently, large spin Hall angle of 0.114 is experimentally observed in Au/FePt system at room temperature [4]. Mainly based on the first-principles band structure calculations, the orbital-dependent Kondo effect of Fe in Au is proposed to explain the nature of the experimentally observed giant spin Hall signals [5]: It has been proposed that the e_g orbitals of Fe are in the Kondo limit and t_{2g} orbitals are in the mixed-valence region. The enhanced spin-orbit interaction by the electron correlation in the t_{2g} orbitals leads to the giant spin Hall effect. While, different opinion on the nature of Kondo effect for Fe in Au is also proposed [6]: They suggest an effective spin-3/2 3-channel Kondo model, involving local and band electrons of t_{2g} symmetry.

It is important, therefore, to develop methods which could treat correlations and the quantum spin fluctuation of Fe impurities correctly. In this paper, we take a two-step calculations to describe an Fe impurity in the face centered cubic (FCC) Au host. First, a single-impurity and two-orbital Anderson model [7] is formulated within the density functional theory (DFT) [8] for determining the host band structure, the impurity energy levels, and the impurity-host hybridization. Second, the magnetic behaviors of the Anderson impurity model at finite temperatures are calculated by the Hirsch-Fye quantum Monte Carlo (QMC) technique [9].

By such unbiased calculation, we should be able to draw useful conclusion about the orbital-dependent Kondo effect for Fe in Au.

A single-impurity and multi-orbital Anderson model is defined as

$$H_0 = \sum_{\mathbf{k},\alpha,\sigma} \epsilon_\alpha(\mathbf{k}) c^\dagger_{\mathbf{k}\alpha\sigma} c_{\mathbf{k}\alpha\sigma} + \sum_{\mathbf{k},\alpha,\xi,\sigma} (V_{\xi\mathbf{k}\alpha} d^\dagger_{\xi\sigma} c_{\mathbf{k}\alpha\sigma} + H.c.) + \sum_{\xi,\sigma} \epsilon_\xi d^\dagger_{\xi\sigma} d_{\xi\sigma} \quad (1)$$

$$H = H_0 + U \sum_\xi n_{\xi\uparrow} n_{\xi\downarrow} + \frac{U'}{2} \sum_{\xi\neq\xi',\sigma,\sigma'} n_{\xi\sigma} n_{\xi'\sigma'} - \frac{J}{2} \sum_{\xi\neq\xi',\sigma} n_{\xi\sigma} n_{\xi'\sigma}, \quad (2)$$

where $c^\dagger_{\mathbf{k}\alpha\sigma}$ ($c_{\mathbf{k}\alpha\sigma}$) is the creation (annihilation) operator for a host electron with wavevector $\mathbf{k}$ and spin σ in the band α, and $d^\dagger_{\xi\sigma}$ ($d_{\xi\sigma}$) is the creation (annihilation) operator for a localized electron at the impurity orbital ξ ($\xi = xz$, yz, xy, z^2, x^2-y^2) and spin σ with $n_{\xi\sigma} = d^\dagger_{\xi\sigma} d_{\xi\sigma}$. For the Au host energy band $\epsilon_\alpha(\mathbf{k})$, the Fe impurity ξ orbital energy ϵ_ξ, and the impurity-host hybridization $V_{\xi\mathbf{k}\alpha}$, these one-body interactions will be calculated by the DFT code QUANTUM-ESPRESSO[11] in nonmagnetic case. U (U') is the on-site Coulomb repulsion within (between) the orbitals of the impurity, and J is the Hund-type coupling between the orbitals of the impurity. Considering the parameters used in the previous calculations for Fe in Au [5], and the relationship $U = U' + 2J$ [10], here we use the following values: $U = 5$, $U' = 3.2$, and $J = 0.9$ eV, and these many-body interactions will be treated by the QMC calculations. It is noted that, compared with the dominant Coulomb U and U' terms, the spin-flip parts of the Hund J terms are omitted in Eq. (2) to avoid possible sign problem in QMC calculations.

Figure 1 shows our DFT results of the band structure for FCC Au, where the Fermi energy is set as zero. In our calculation, the exchange-correlation interactions are described by the Perdew-Zunger local density approximation (LDA), and the electron-ion interactions are represented by the the Rabe-Rappe-Kaxiras-Joannopoulos ultrasoft pseudopotentials [12]. The optimized lattice constance is $a = 7.643$ Bohr, in good agreement with the experimental value 7.67 Bohr [13]. 9 orbitals (one $6s$, three $6p$, and five $5d$) are included for Au atom.

The hybridization matrix element between Fe impurity and Au host $V_{\xi\mathbf{k}\alpha} \equiv \langle\varphi_\xi|H_0|\Psi_\alpha(\mathbf{k})\rangle$ has the form of

$$V_{\xi\mathbf{k}\alpha} = \frac{1}{\sqrt{N}} \sum_{p,\mathbf{n}} e^{i\mathbf{k}\cdot\mathbf{n}} a_{\alpha p}(\mathbf{k}) \langle\varphi_\xi|H_0|\varphi_p(\mathbf{n})\rangle, \quad (3)$$

where H_0 is defined in Eq. (1), φ_ξ is the ξ state of Fe impurity, and $\Psi_\alpha(\mathbf{k})$ is the Au host state with wavevector $\mathbf{k}$ and band index α, which is expanded by atomic orbitals $\varphi_p(\mathbf{n})$ with orbital index p and site index $\mathbf{n}$, and $a_{\alpha p}(\mathbf{k})$ are expansion coefficients. To calculate the mixing integrals $\langle\varphi_\xi|H_0|\varphi_p(\mathbf{n})\rangle$, let's consider a FCC supercell $Au_{26}Fe$, which consists of 3×3×3 FCC primitive cells, where each primitive cell consists of one Au atom, and a Au atom located at the center of the supercell is replaced by an Fe atom. Figure 2 shows the impurity-host hybridization calculated from Eq.(3) with the above parameters, where the hybridization function is defined by $\overline{V}_\xi(\mathbf{k}) \equiv (\sum_\alpha |V_{\xi\mathbf{k}\alpha}|^2)^{1/2}$, and the summation over α is performed over α=9 conduction bands of host Au. Here, $\overline{V}_\xi(\mathbf{k})$ is plotted along various directions in the Brillouin zone for FCC structure. It is observed that, at the Γ point ($\mathbf{k}$=0), the hybridization value $\overline{V}_\xi(\mathbf{k} = 0)$ for the $\xi = e_g$(z^2,x^2-y^2) orbitals of Fe impurity is smaller than that for the $\xi = t_{2g}$ (xz,yz,xy) orbitals.

Using the above DFT results for the supercell $Au_{26}Fe$ in nonmagnetic case, it could roughly tell us the energy levels of the Fe impurity: $\epsilon_\xi \approx$ -1.9 eV for $\xi = e_g$ (z^2, x^2-y^2), and $\epsilon_\xi \approx$ -1.8 eV for $\xi = t_{2g}$ (xz,yz,xy), where the Fermi energy is set as zero. It is noted that the result of the impurity energy levels is consistent with the result of the impurity-host hybridization in Fig.2: the lower impurity level, the smaller impurity-host hybridization value (at Γ point).

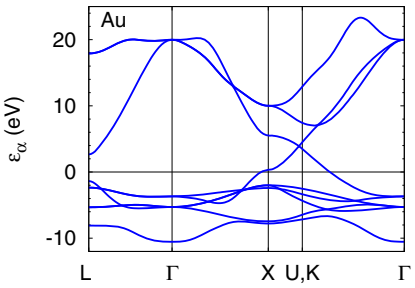

Figure 1. (Color online) Energy bands of Au with face centered cubic structure.

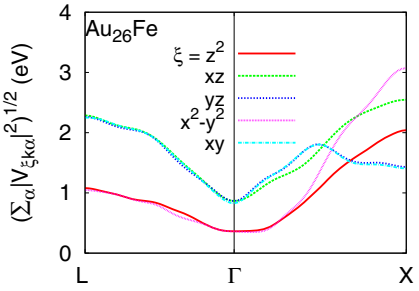

Figure 2. (Color online) Hybridization between ξ orbitals of Fe impurity and Au host metal.

Next, the magnetic behavior of the Fe impurity is studied by the Hirsch-Fye QMC technique [9]. Owing to calculation constraints, we simplified to a two-orbital model with one e_g and one t_{2g} orbitals in order to study the essentially different behaviors of e_g and t_{2g} orbitals. The e_g (t_{2g}) orbital is arbitrarily chosen as z^2 (xz) orbital. The following results are obtained with more than 10^5 Monte Carlo sweeps and Matsubara time step $\Delta\tau = 0.25$.

Figure 3 shows the temperature dependence of (a) the square of magnetic moment $\langle (M_\xi^z)^2 \rangle$, (b) the susceptibility times temperature $T\chi_\xi$, and (c) the occupation number $\langle n_\xi \rangle$, which are defined as

$$M_\xi^z = n_{\xi\uparrow} - n_{\xi\downarrow}, \tag{4}$$

$$\chi_\xi = \int_0^\beta d\tau \langle M_\xi^z(\tau) M_\xi^z(0) \rangle, \tag{5}$$

$$n_\xi = n_{\xi\uparrow} + n_{\xi\downarrow}, \tag{6}$$

respectively. The open squares and circles are the QMC results for the ξ orbitals of Fe impurity in Au host, where the impurity energy levels ϵ_ξ= -1.9 (ξ=z^2) and -1.8 eV (ξ=xz) are taken from the above DFT calculation for the supercell $Au_{26}Fe$ in nonmagnetic case. It is found that, being the lower energy level, the $e_g(z^2)$ orbital has the larger magnetic moment, the much larger susceptibility with much smaller Kondo temperature [14], and the larger occupation number. In contrast, being the higher energy level, the $t_{2g}(xz)$ orbital has the smaller magnetic moment, the much smaller susceptibility with much larger Kondo temperature, and the smaller occupation number. Thus, for Fe impurity in Au host, the orbital-dependent Kondo effect is directly and clearly manifested, where the Kondo temperature of the e_g orbital is found to be much lower than that of the t_{2g} orbital. Our QMC results support the previous viewpoint of Guo, Maekawa, and Nagaosa[5].

To study what will happen if the energy levels of the e_g and t_{2g} orbitals are degenerate, figure 4 shows the QMC results for the Fe impurity in Au host, which is the same as what we have done in Figure 3, except that here the impurity energy levels are taken as ϵ_ξ= -1.85 eV for ξ=z^2 and xz, the average value used in Figure 3. Here, nearly the same behaviors are observed. For the $e_g(t_{2g})$ orbital, it has the larger (smaller) magnetic moment, the lager (smaller) susceptibility with smaller (larger) Kondo temperature, and the larger (smaller) occupation number. Thus, it is clearly shown that the difference of impurity-host hybridization is more important than the difference of impurity energy levels to induce the orbital-dependent Kondo effect.

To conclude, we have studied the orbital-dependent Kondo effect for an Fe impurity in Au host by a combined approach of density functional theory and quantum Monte Carlo method. Our results show that the Kondo temperature of e_g electrons is much lower than that of t_{2g}

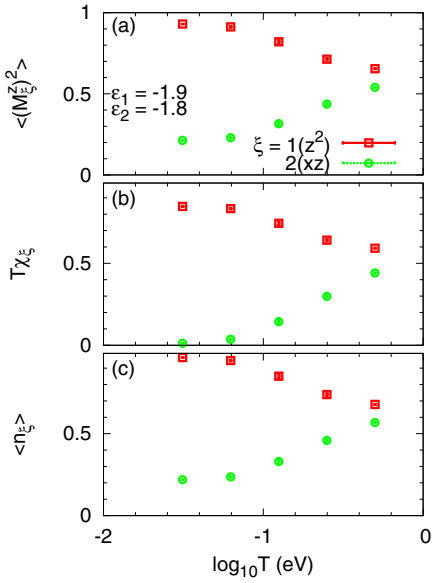

Figure 3. (Color online) Temperature dependence of (a) square of magnetic moment $\langle (M_\xi^z)^2 \rangle$, (b) susceptibility $T\chi_\xi$, and (c) occupation number $\langle n_\xi \rangle$ for Fe impurity in Au.

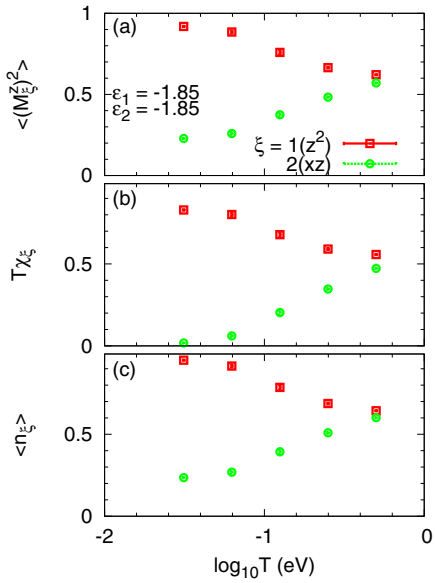

Figure 4. (Color online) Same as Figure 3, except that here the impurity energy levels are taken as ϵ_ξ= -1.85 eV for ξ=z^2 and xz, the average value used in Figure 3.

electrons of Fe atoms, and thus support the previous viewpoint of Guo, Maekawa, and Nagaosa [5]. In addition, it is found that the difference of impurity-host hybridization is more important than the difference of impurity energy levels to induce the orbital-dependent Kondo effect.

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[14] For a fixed T (higher than Kondo temperature T_K), the larger $T\chi$ is, the lower T_K is needed to decrease $T\chi$ into zero.