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PHYSICAL REVIEW LETTERS

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Enhanced Spin Hall Effect by Resonant Skew Scattering in the Orbital-Dependent Kondo Effect

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The enhanced spin Hall effect in Au metal due to the resonant skew scattering is studied with first-principles band structure calculations. Especially the gigantic spin Hall angle $\gamma_S \cong 0.1$ observed recently [T. Seki *et al.*, Nature Mater. **7**, 125 (2008)] is attributed to the orbital-dependent Kondo effect of Fe in the Au host metal, where the t_{2g} orbitals are in the mixed-valence region while e_g orbitals are in the Kondo limit. The enhanced spin-orbit interaction by the electron correlation in the t_{2g} orbitals leads to the gigantic spin Hall effect. Impurities with $5d$ orbitals are also discussed.

Spin Hall effect (SHE) is an effect where the transverse spin current is produced by the electric field or electric current [1–15]. It does not require any magnetic field or magnets, and is an interesting and promising phenomenon for application to spin injection and manipulation in spin-tronics. SHE is especially robust and large in metals due to the large number of carriers and Fermi energy [10–15]. For example, SHE in Pt metal even at room temperature [12,14] is more than 2 orders of magnitude larger than that of GaAs [7]. Even larger SHE has been recently reported in the Au/FePt system [13], where the spin Hall conductivity is $\sim 10^5 \Omega^{-1}$ cm^{-1} and the spin Hall angle γ_S is as large as $\cong 0.1$.

Naively speaking, SHE is the two copies of anomalous Hall effect (AHE) for up and down spins, respectively, and the knowledge on the latter can be directly transferred to the former. When the longitudinal conductivity σ_{xx} is larger than $\sim 10^6 \Omega^{-1}$ cm^{-1}, and the Hall conductivity σ_H is much larger than $e^2/(ha) \cong 10^3 \Omega^{-1}$ cm^{-1} with h and a being the Planck constant and the lattice constant, respectively, the dominant contribution to the AHE is the extrinsic skew scattering [16–20]. In this case, σ_H is proportional to σ_{xx}, and hence the Hall angle $\gamma = \sigma_H/\sigma_{xx}$ is the well-defined measure for the magnitude of AHE independent of the impurity concentration. In other words, the Hall angle can be determined by examining the single scattering event due to the impurity. The typical value of γ is estimated as the ratio $\sim \lambda/\varepsilon_F$ with λ being the spin-orbit interaction (SOI) and ε_F the Fermi energy. Usually, ε_F is at least a few eV, the λ is of the order of 10–20 meV for the $3d$ orbitals, for example. Therefore, the Hall angle is roughly estimated as $\gamma \sim 10^{-3}$. This Hall angle γ can be enhanced by the resonant skew scattering by the magnetic impurity [17,18]. Using the Anderson Hamiltonian describing the virtual bound state causing the resonant scattering, the anomalous Hall angle can be expressed in terms of the hybridization energy Δ and SOI

λ, and the phase shift δ_1 due to the p-wave scattering as $\gamma \sim (\lambda/\Delta) \sin \delta_1$, which can be of the order of 10^{-2} [17]. Therefore, the spin Hall angle $\gamma_S \cong 0.1$ is a surprisingly large value, which needs to be understood for the design of the gigantic SHE.

In this Letter, we propose that the local electron correlation and spin fluctuation further enhance SHE compared with AHE by the explicit first-principles band structure calculation with the Au metal as the host where the Fermi energy is at the $6s$ bands. Namely, SHE is not the simple two copies of AHE, and the comparison between these two offers a unique opportunity to study the many-body effect.

Let us consider the scattering of a spin $S = \frac{1}{2}$ particle by a potential with SOI. The amplitude of the scattered wave is given by [16]

$$f_\uparrow(\theta) = f_1(\theta)|\uparrow\rangle + ie^{i\varphi}f_2(\theta)|\downarrow\rangle,$$
$$f_\downarrow(\theta) = f_1(\theta)|\downarrow\rangle - ie^{-i\varphi}f_2(\theta)|\uparrow\rangle \tag{1}$$

for incoming up-spin and down-spin electrons, respectively, where θ is the angle between the wave vectors of incident ($\vec{k}$) and scattered ($\vec{k}'$) waves, and $f_1(\theta)(f_2(\theta))$ corresponds to the spin nonflip (spin flip) scattering am-
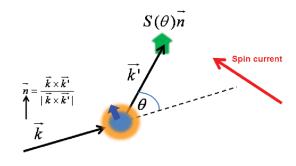

FIG. 1 (color). The spin polarization $S(\theta)\vec{n}$ induced by the skew scattering due to the spin-orbit interaction of the scatterer and the spin unpolarized electron beam.

plitudes. The skewness of the scattering is represented by the function $S(\theta) = \frac{2\mathrm{Im}[f_1^*(\theta)f_2(\theta)]}{|f_1(\theta)|^2 + |f_2(\theta)|^2}$, while the function $I(\theta) = |f_1(\theta)|^2 + f_2(\theta)|^2$ determines the scattering intensity. The meaning of the skewness function $S(\theta)$ is shown in Fig. 1. When the unpolarized electrons are incident, the scattered electrons are spin polarized as $S(\theta)\vec{n}$ with $\vec{n} = (\vec{k} \times \vec{k}')/|\vec{k} \times \vec{k}'|$. By solving the Boltzmann equation with this skew scattering, the spin Hall angle γ_S is given by [9] $\gamma_S = \frac{\int d\Omega I(\theta)S(\theta)\sin\theta}{\int d\Omega I(\theta)(1-\cos\theta)}$, where $\int d\Omega$ is the integral over the solid angle. The numerator represents the transverse spin current produced by the scattering, i.e., the velocity perpendicular both to $\vec{k}$ and $\vec{n}$ with the spin polarized along $\vec{n}$, while the denominator corresponds to the usual transport scattering rate. Without the resonance effect, the typical value of γ is of the order of 10^{-3}, i.e., much smaller than unity. Actually, the obtained value of γ in Ref. [9] is $1/500$ for n-type GaAs assuming the screened Coulomb potential. The partial wave analysis gives the expression for $f_1(\theta)$ and $f_2(\theta)$

$$f_1(\theta) = \sum_l \frac{P_l(\cos\theta)}{2ik}[(l+1)(e^{2i\delta_l^+} - 1) + l(e^{2i\delta_l^-} - 1)],$$

$$f_2(\theta) = \sum_l \frac{\sin\theta}{2ik}(e^{2i\delta_l^+} - e^{2i\delta_l^-})\frac{d}{d\cos\theta}P_l(\cos\theta). \tag{2}$$

Putting Eq. (2) into the expression for γ_S above, we obtain

$$\gamma_S = \frac{3\mathrm{Im}[(e^{-2i\delta_1} - 1)(e^{2i\delta_2^+} - e^{2i\delta_2^-})]}{9\sin^2\delta_2^+ + 4\sin^2\delta_2^- + 3[2 - \cos 2\delta_2^+ - \cos 2\delta_2^-]}, \tag{3}$$

where we have assumed that the resonant channel is the d wave ($l = 2$) which is subject to SOI and the scattering is characterized by the two phase shifts $\delta_2^\pm = \delta_{J=2\pm1/2}$, while that ($\delta_1$) for the p-wave scattering is assumed to be spin independent. Assuming that δ_1 for the nonresonant p wave is small ($|\delta_1| \cong 0.1$ [17]), $\gamma_S \cong -6\delta_1(\cos 2\delta_2^+ - \cos 2\delta_2^-)/(9\sin^2\delta_2^+ + 4\sin^2\delta_2^- + 3[2 - \cos 2\delta_2^+ - \cos 2\delta_2^-])$. Thus, the most important factor is $\cos 2\delta_2^+ - \cos 2\delta_2^-$, which is related to the difference in the occupation numbers of the $J = 2 \pm \frac{1}{2}$ impurity states induced by SOI through the Friedel sum rule [21]. Thus, the local density of states (DOS) for the d electrons determines the magnitude of SHE, which can be studied by the first-principles calculation as described below.

We take Au as the host metal, where the gigantic SHE has been observed [13]. The electron configuration of Au atom is $5d^{10}6s^1$, and the Fermi energy is at the $6s6p$ bands with relatively small SOI. Therefore, it is difficult to explain the giant SHE in terms of the intrinsic mechanism, in sharp contrast to the case of Pt with $5d^96s^2$ [14]. Because in [13] the spin current is supplied from FePt to Au, it is natural to consider the three possibilities of the imperfections, i.e., (i) Au vacancies, (ii) Pt impurities, and (iii) Fe impurities. From the above consideration, there are several requirements to obtain the gigantic SHE; (I) there should

be the resonance at the Fermi energy due to either the Kondo peak or the mixed valance, (II) the orbital angular momentum should not be quenched, and (III) the peak must be split due to SOI by the energy comparable or larger than the width of the peak. We have studied the impurity states in Au host metal for these three cases in terms of the local density approximation (LDA)[22] plus on-site Coulomb interaction U (LDA + U) [23] ($U = 5$, $J = 0.9$ eV). We used the accurate full-potential augmented plane wave method, as implemented in the WIEN2K code [24]. The atomic positions are relaxed in the presence of the impurity. The numerical results presented below have been tested for convergence with respect to the energy cutoff for augmented plane waves, k points used for irreducible Brillouin zone and supercell size. Figure 2 shows the DOS in the presence of one impurity in the $2 \times 2 \times 2$ supercell. Basically the structure extending from -8 to -2 eV is due to the $5d$ bands of Au, while $6s6p$ bands of Au are extended all through in this energy range with smaller DOS. The change in the DOS is almost confined in the range of the $5d$ bands in the case of (i) vacancy [Fig. 2(a)], and is at around -1.5 eV in the case of (ii) Pt [Fig. 2(b)]. We could not obtain a magnetic state
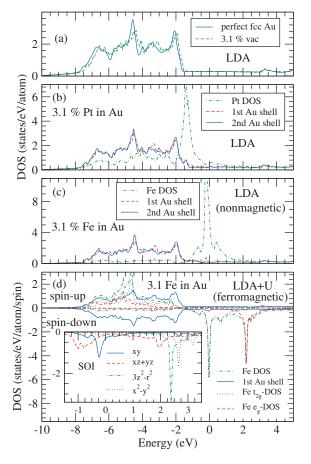

FIG. 2 (color). Total, site-, orbital- and spin-decomposed DOSs of (a) bulk fcc Au, 3.1% Au-vacancies, (b) 3.1% Pt impurities, (c) 3.1% Fe impurities in nonmagnetic state, and (d) in ferromagnetic state.

in these cases even in the LDA + U calculation. This conclusion is consistent with the earlier study by photoelectron spectroscopy [25]. In sharp contrast, we obtained the magnetic state as the ground state with both the LDA and LDA + U calculations in the case of Fe. Accordingly, the DOS for Fe [Fig. 2(d)] shows the spin splitting, and the down-spin DOS has the sharp peak close to the Fermi energy. (We put the DOS for nonmagnetic state in Fig. 2(c) for reference.) This means that there occurs the valence fluctuation of Fe ion between d^6 and d^7. This is reasonable since the Fe in Au is known as a Kondo impurity but the Kondo temperature is as low as 0.4 K. Thus, we conclude that only (iii) Fe impurities could be the origin of the large SHE satisfying the criteria (I), (II), (III) discussed above.

The band structure calculation for the state with local magnetic and orbital orderings corresponds to the mean field theory of the Anderson Hamiltonian [21]. In the limit of isolated impurity atom, this mean field theory gives the correct energy positions of the peaks in the spectral function of the single-particle Green's function. Of course, there is no symmetry breaking by the local electron correlation, and the true ground state is the superposition of the degenerate symmetry breaking states, i.e., quantum fluctuation of spins and orbitals occur. Early theories of Kondo effect of Fe in Au have estimated the relevant quantities as $\Delta \cong 1.4$ eV, $U \cong 5.4$ eV, $J \cong 0.9$ eV [26], where Δ is the energy broadening of the virtual bound state due to the hybridization with the conduction bands. The crystal field splitting is considered to be small (~ 0.1 eV), and SOI $\lambda \cong 30$ meV is even smaller. The resistivity measurement at room temperature shows a systematic change as the valence of the impurity changes as Ti, V, Cr, Mn, Fe, Co, Ni, and shows the dip at Mn, while the maximum at Fe (Fig. 17 of Ref. [27]). This strongly suggests the peak in the DOS for Fe, i.e., the mixed valence case, although the low temperature properties have been analyzed by the Kondo model [27]. The magnetic susceptibility measurement shows the $S = 2$ magnetic moment, while the Mössbauer experiment concluded rather $S = \frac{3}{2}$ [28]. These somewhat confusing situation can be resolved by the LDOS in Figs. 2(c) and 2(d) together with Table I. Table I shows the calculated spin/orbital magnetic moments and the d-orbital occupation numbers. Note that the obtained values depend slightly on the muffin-tin sphere radius $R_{\rm mt}$ and U value, but the semiquantitative conclusion does not change. First, the nonmagnetic state in the LDA calculation shows almost no crystal field splitting (~ 0.1 eV), which is consistent with the earlier result. However, the inclusion of U changes the situation dramatically, and the e_g-t_{2g} splitting is enhanced to be around 2 eV as shown in Fig. 2(d). This corresponds to the orbital polarization due to the electron correlation, i.e., the local version of the orbital ordering not by the crystal field but by the electron correlation. Therefore we conclude that the orbital-dependent Kondo effect occurs for Fe in Au; the e_g orbitals are in the Kondo limit, while t_{2g} orbitals are in the mixed valence region. At

TABLE I. Down-spin occupation numbers of the 3d orbitals of the Fe impurity in Au from LDA + U calculations. The calculated magnetic moments are $m_s^{\rm Fe} = 3.39 \mu_B$ and $m_s^{\rm tot} = 3.32 \mu_B$ without SOI, as well as $m_s^{\rm Fe} = 3.19 \mu_B$, $m_o^{\rm Fe} = 1.54 \mu_B$, and $m_s^{\rm tot} = 3.27 \mu_B$ with SOI. The muffin-tin sphere radius $R_{\rm mt} = 2.65 a_0$ (a_0 is Bohr radius) is used.

(a)	xy	xz	yz	$3z^2 - r^2$	$x^2 - y^2$
No SOI	0.459	0.459	0.459	0.053	0.053
SOI	0.559	0.453	0.453	0.050	0.128
(b)	$m = -2$	$m = -1$	$m = 0$	$m = 1$	$m = 2$
No SOI	0.256	0.459	0.053	0.459	0.256
SOI	0.138	0.087	0.050	0.819	0.549

temperatures above $T_K \cong 0.4$ K, the t_{2g} orbitals, within which the orbital angular momentum is not quenched, play the major role in the transport properties, while the e_g orbitals determine the low temperature Kondo effect.

Now we consider the orbital polarization within the t_{2g} states due to SOI. Note that t_{2g} orbitals behaves like $l_{\rm eff} = 1$ states with xy and $zx \pm iyz$ orbitals corresponding to $m = 0$ and $m = \pm 1$ states, respectively. Thus, SOI is effective within the t_{2g} states leading to the energy splitting between the $J_{\rm eff} = 3/2$ and $J_{\rm eff} = 1/2$ states. Naively, the orbital polarization is determined by the competition between the hybridization energy Δ and the SOI splitting. Here, one must carefully distinguish between the many-body states and the single-particle states. The energy separation between the many-body states with different total angular momentum J is typically the order of SOI, and much smaller than U or J. However, once the many-body ground state of d electrons is fixed, the separation of the single-particle state energy, which is the energy difference between the N-electron and $N \pm 1$-electron state, can be as large as U or J, which is important for the conduction electrons which comes in or out to the d orbitals. Thus, it is possible that the electron correlation U plays an essential role, and even a SOI much smaller than the hybridization energy can produce the large orbital magnetic moment $m_o = 1.5 \mu_B$ as shown in Table I. Correspondingly, the single-particle $m = 1$ state is almost occupied (0.82) while $m = -1$ state is almost empty (0.09), as is seen also from the inset of Fig. 2(d). Figure 2(d) and Table I also explain why the AHE is rather small compared with SHE. As for AHE, the phase shift for $m = 1$ ($m = -1$) are almost π (0), and both of them do contribute a little to the scattering, while the $m = 0$ state is almost in the unitary limit with $\pi/2$-phase shift. Thus, we do not expect the enhanced AHE, leading to the small anomalous Hall angle compared with that for SHE [17]. For the SHE, on the other hand, such a cancellation does not occur. One needs to treat the spin or orbital fluctuation in this case, but a rough estimate for the spin Hall angle can be obtained as follows. For the conduction electrons, the energy difference between $J_{\rm eff} = 3/2$ and $J_{\rm eff} = \frac{1}{2}$ is that of $m = 1$ and $m = -1$ states in the mean field theory when one considers the Ising type cou-
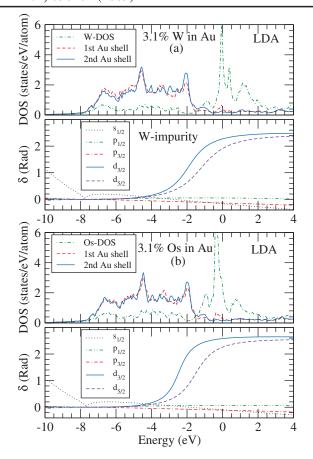
FIG. 3 (color). Site-decomposed DOSs and phase shifts (δ) of (a) 3.1% W and (b) 3.1% Os in Au.

pling $l_z s_z$. This energy is larger than the hybridization energy and we expect the difference of the phase shifts between these two channels of the order of π, giving a large spin Hall angle of the order of $\delta_1 \cong 0.1$ as observed experimentally [13]. This picture for the Kondo effect in Fe impurity in Au is different from the conventional one [26]. Further experimental studies using the spectroscopies such as STS and ARPES are highly desired to clarify the nature of this fundamental problem.

SHE associated with Kondo effect is expected for other ions such as rare earths [29]. We have also studied the case of 5d metals (Ta, W, Re, Os, Ir) doped into Au. In these cases, the appropriate U value is ~0.5 eV, and there occurs no magnetic state. However, SOI is almost as large as U, and hence the large SHE is expected. The DOS and the associated phase shifts for W and Os are shown in Fig. 3 as the two representatives. Even without the magnetic moment, SHE is enhanced due to the resonant state at Fermi energy, and the corresponding spin Hall angle is estimated as $\gamma_S \cong 0.2 \sin 2\delta_1 \cong 0.04$ in these cases, in semiquantitative agreement with the early experiment [17].

In conclusion, we have studied the enhanced SHE due to the resonant skew scattering. Compared with AHE, SHE, where the time-reversal symmetry is not broken, gives a unique opportunity to study the electronic states near the impurity without disturbing its magnetic behavior. We have presented the formula for the spin Hall angle in terms of the phase shifts [Eq. (3)], and also the first-principles band structure calculation to analyze the mechanism of the gigantic SHE. We have shown that SHE shed a new light on the Kondo effect, which plays the key role to enhance SHE and a new picture for the Fe impurity state in Au has been proposed. This leads to the material design of the large SHE even at room temperature with the potential application to the spintronics.

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