Sign Change of the Spin Hall Effect due to Electron Correlation in Nonmagnetic CuIr Alloys

Zhuo Xu,1,2 Bo Gu,1,2 Michiyasu Mori,1,2 Timothy Ziman,3,4 and Sadamichi Maekawa1,2
1Advanced Science Research Center, Japan Atomic Energy Agency, Tokai 319-1195, Japan
2CREST, Japan Science and Technology Agency, Sanbancho, Tokyo 102-0075, Japan
3Institut Laue Langevin, Boîte Postale 156, F-38042 Grenoble Cedex 9, France
4LPMMC (UMR 5493), Université Grenoble 1 and CNRS, 38042 Grenoble, France

(Received 28 May 2014; published 6 January 2015)

Recently, a positive spin Hall angle (SHA) of 0.021 was observed experimentally in nonmagnetic CuIr alloys [Niami et al, Phys. Rev. Lett. 106, 126601 (2011)] and attributed predominantly to an extrinsic skew scattering mechanism, while a negative SHA was obtained from ab initio calculations [Fedorov et al, Phys. Rev. B 88, 085116 (2013)], using consistent definitions of the SHA. We reconsider the SHA in CuIr alloys, with the effects of the local electron correlation $U$ in 5$d$ orbitals of Ir impurities, included by the quantum Monte Carlo method. We found that the SHA is negative if we ignore such local electron correlation, but becomes positive once $U$ approaches a realistic value. This may open up a way to control the sign of the SHA by manipulating the occupation number of impurities.

The spin Hall effect, which converts charge current into spin current via the spin-orbit interaction (SOI), is one of the key phenomena for the further development of spintronics devices [1,2]. The spin Hall angle (SHA) describes the conversion efficiency from the injected longitudinal charge current into the scattered transverse spin current. Recently, a positive SHA of 2.1% was measured in nonmagnetic CuIr alloys [3] and argued to be predominantly due to extrinsic skew scattering, while negative SHAs of $-0.035$ and $-0.029$ were calculated for CuIr alloys, from the Boltzmann equation and the Kubo-Streda formula, respectively [4], with consistent definitions [5,6]. The spin Hall effect in CuIr alloys in experiment is mainly due to skew scattering [3], which is well described by the phase-shift model of Fert and Levy [7,8]. According to this model, the SHA is proportional to the phase shift parameter $\delta_1$, which was originally taken to be $|\delta_1| = 0.1$ [7,8]. It is given as $\delta_1 = \pi(N_{6p}^{Ir} - N_{6p}^{Cu})/6$, where $N_{6p}^{Ir}$ and $N_{6p}^{Cu}$ are the occupation numbers for the 6$p$ orbitals around an Ir impurity and the 4$p$ orbitals of Cu host, respectively. In the atomic limit, $N_{6p}^{Ir} = N_{6p}^{Cu} = 0$, while in the CuIr alloys $N_{6p}^{Ir}$ and $N_{6p}^{Cu}$ become finite, but small, due to the mixing with the other orbitals. To predict the sign of the SHA in CuIr alloys, therefore, we need to precisely calculate the sign of $\delta_1$ [7,8].

In this Letter, we argue that the question of the sign of the phase shift parameter $\delta_1$ and the SHA in CuIr alloys is highly nontrivial. Our idea is shown schematically in Fig. 1. The nonmagnetic CuIr alloys can be described by an Anderson impurity model [9], where Ir is an impurity. In a simplified Anderson model within the Hartree-Fock approximation, it is clear that, due to the on-site Coulomb correlation $U$, the impurity level increases, while the impurity occupation number decreases [9].

For Ir impurities in Cu, we define the occupation numbers of the 5$d$ ($N_{6d}^{Ir}$), 6$s$ ($N_{6s}^{Ir}$), and 6$p$ ($N_{6p}^{Ir}$) states to be projections of the occupied electronic states onto the impurity states of corresponding symmetry centered on the substitutional atomic site

$$N_{s,p,d}^{Ir} = \int_{-\infty}^{E_f} \rho_{s,p,d}^{Ir}(e)de.$$  \hspace{1cm} (1)

![FIG. 1 (color online). Schematic picture of the density of states (DOS) of spin-up and spin-down electrons, in the nonmagnetic CuIr alloys. The DOS of Ir 5$d$ orbitals are shown by the outer curves for the on-site Coulomb repulsion $U = 0$ (black) and $U > 0$ (red), respectively. $\epsilon_d$ is the impurity level in the Hartree-Fock approximation. The occupation number of Ir 5$d$ decreases as the correlation $U$ increases.](Image)
This constraint is respected by our density functional theory (DFT) calculation (see later).

According to the Friedel sum rule, the phase shifts \( \delta \) can be calculated by the occupation numbers of the corresponding orbitals as \([10,11]\)

\[
\begin{align*}
\delta_1 &= \delta_p^+ - \delta_p^- = \frac{\pi (N_{p}^I - N_{p}^{Cu})}{6}, \\
\delta_2^+ &= \delta_{d+}^+ - \delta_{d+}^- = \frac{\pi (N_{d+}^I - N_{d+}^{Cu})}{6}, \\
\delta_2^- &= \delta_{d-}^- - \delta_{d-}^+ = \frac{\pi (N_{d-}^I - N_{d-}^{Cu})}{4}.
\end{align*}
\]

When the correlation \( U \) is included into the 5d states of the Ir impurity, the decreased \( N_{p}^I \) is accompanied by increased \( N_{d+}^I \) and \( N_{d-}^I \), according to Eq. (2). By Eq. (3), a negative \( \delta_1 \) (\( \sim N_{p}^I - N_{p}^{Cu} \)) may change sign and become positive, due to the increased \( N_{d+}^I \). This will be confirmed by the calculations in the following sections.

**Spin Hall angle due to impurities of d orbitals.**—For an electron scattered by a potential with the SOI, the amplitudes of the scattered wave are given by \([5,12]\)

\[
\begin{align*}
f_{\uparrow}(\theta) &= f_1(\theta) |\uparrow\rangle + e^{i\varphi} f_2(\theta) |\downarrow\rangle, \\
f_{\downarrow}(\theta) &= f_1(\theta) |\downarrow\rangle - e^{-i\varphi} f_2(\theta) |\uparrow\rangle,
\end{align*}
\]

for incoming spin-up and spin-down electrons. \( f_1(\theta) \) and \( f_2(\theta) \) represent the spin nonflip and spin flip scattering amplitudes, respectively. \( \theta \) and \( \varphi \) are the polar and azimuthal angles of the scattered wave vector. The scattering amplitudes can be expressed in terms of the phase shifts \( \delta_l \) of the orbitals \( l \) as

\[
\begin{align*}
f_1(\theta) &= \sum_l \frac{P_l(\cos \theta)}{2l!} [(l + 1)(e^{2i\delta_l^\uparrow} - 1) + l(e^{2i\delta_l^\downarrow} - 1)], \\
f_2(\theta) &= \sum_l \frac{-\sin \theta}{2l!} (e^{2i\delta_l^\downarrow} - e^{2i\delta_l^\uparrow}) \frac{d}{d \cos \theta} P_l(\cos \theta),
\end{align*}
\]

with the two phase shifts \( \delta_l^\uparrow = \delta_l^\downarrow(1/2) \) differing because of spin-orbit terms; without them \( \delta_l^\uparrow = \delta_l^\downarrow = \delta_l \).

The spin-independent part \( I(\theta) \) and skewness \( S(\theta) \) of the scattering cross section are represented by

\[
\begin{align*}
I(\theta) &= |f_1(\theta)|^2 + |f_2(\theta)|^2, \\
S(\theta) &= \frac{2 \text{Im}[f_1(\theta)f_2(\theta)]}{|f_1(\theta)|^2 + |f_2(\theta)|^2},
\end{align*}
\]

and the transport skewness \( \gamma_k \) is defined as \([13]\)

\[
\gamma_k = \int d\Omega(\theta) S(\theta) \sin \theta \
\int d\Omega(\theta)(1 - \cos \theta).
\]

The SHA \( \alpha \) can be defined either by conductivity \( \sigma \) or by resistivity \( \rho \) as \([5,13]\)

\[
\begin{align*}
\alpha(\sigma) &= \sigma_{xx}^{(+)} / \sigma_{xx}^{(+)} = \frac{\gamma_k}{2}, \\
\alpha(\rho) &= \rho_{xx}^{(+)} / \rho_{xx}^{(+)} = -\alpha(\sigma).
\end{align*}
\]

We note that it was \( \alpha(\rho) \) that was measured in the experiment of Ir doped in Cu \([3]\), while \( \alpha(\sigma) \) was calculated in the previous theory \([4]\). Using consistent definitions, the SHA in Ref. \([4]\) is opposite in sign to the experimental value of Ref. \([3]\).

For the nonmagnetic impurity Ir as an extrinsic scatterer in Cu, the skew scattering arises from the interference between the antisymmetric scattering of \( l = 2 \) and the symmetric scattering of \( l = 1 \) channels \([8]\). It is assumed that only the \( d \)-wave scattering is the resonant channel with appreciable SOI, while the \( p \) wave is taken spin independent. Then, substituting Eq. (5) with parameters of \( \delta_1, \delta_2^+, \) and \( \delta_2^- \) into Eq. (9), the SHA is obtained as

\[
\alpha(\rho) = -\frac{6 \sin \delta_1 [\sin(\delta_2^+ - \delta_1) \sin \delta_2^- - \sin(\delta_2^- - \delta_1) \sin \delta_2^+] }{5(3 \sin^2 \delta_2^+ + 2 \sin^2 \delta_2^-)}.
\]

We note that a factor 1/2 was missing from the equation for the SHA due to skew scattering of \( d \) orbitals in Refs. \([14–16]\), and the quoted numerical results for that angle should have been divided by 2.

**LDA + SOI results.**—We now calculate the phase shift parameters \( \delta_1, \delta_2^+, \) and \( \delta_2^- \) for the Ir impurity doped in Cu host based on DFT with the local density approximation (LDA) plus SOI. We use the code of QUANTUM ESPRESSO (QE) \([17]\) with Hubbard \( U = 0 \). A supercell of Cu_{8}Ir was used to calculate the occupation numbers of the orbitals around the Ir impurity, while the primitive cell of a single Cu atom gave the occupation numbers of the orbitals of the Cu host. The cutoff energy is 50 Ry for ultrasoft pseudopotentials with the Perdew-Burke-Ernzerhof type of exchange-correlation functionals \([18]\), and the energy convergence limit is \( 10^{-8} \) Ry, with a \( k \) lattice of \( 8 \times 8 \times 8 \).

From these calculations for \( U = 0 \), the occupation numbers, phase shifts, and SHA are listed in Table I. The total occupation number of Ir with 5d, 6s, and 6p states
TABLE I. Occupation numbers (N), phase shifts (δ), and calculated SHA for an Ir impurity in a Cu host, with local electron correlation U on the 5d orbitals of Ir varying from 0 to 0.5 eV. For U = 0 (first line, in boldface), the occupation numbers are calculated with LDA + SOI by DFT, which also gave N^Cu^0 = 0.96 and N^Ir^0 = 9.68 for the Cu host. For U > 0, N^d_i, δ^d_i, and δ^σ_i are calculated by the QMC method. N^d_i and N^σ_i are then estimated from Eq. (2), (keeping the ratio N^d_i/N^σ_i as for U = 0. For each value of U the phase shift δ_i follows from the Friedel sum rule, Eq. (3) and the SHA from Eq. (10) in the text.

<table>
<thead>
<tr>
<th>U (eV)</th>
<th>N^d^0_i</th>
<th>δ^d_i</th>
<th>δ^σ_i</th>
<th>N^d^U</th>
<th>N^σ^U</th>
<th>δ^σ_i</th>
<th>SHA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.82</td>
<td>-0.73</td>
<td>-0.38</td>
<td>0.32</td>
<td>0.86</td>
<td>-0.05</td>
<td>-1.1%</td>
</tr>
<tr>
<td>0.1</td>
<td>7.50</td>
<td>-0.76</td>
<td>-0.57</td>
<td>0.41</td>
<td>1.09</td>
<td>0.07</td>
<td>+0.8%</td>
</tr>
<tr>
<td>0.2</td>
<td>7.20</td>
<td>-0.89</td>
<td>-0.61</td>
<td>0.49</td>
<td>1.31</td>
<td>0.19</td>
<td>+2.5%</td>
</tr>
<tr>
<td>0.3</td>
<td>6.82</td>
<td>-1.06</td>
<td>-0.65</td>
<td>0.59</td>
<td>1.59</td>
<td>0.33</td>
<td>+4.6%</td>
</tr>
<tr>
<td>0.4</td>
<td>6.38</td>
<td>-1.26</td>
<td>-0.70</td>
<td>0.70</td>
<td>1.92</td>
<td>0.50</td>
<td>+5.4%</td>
</tr>
<tr>
<td>0.5</td>
<td>5.96</td>
<td>-1.45</td>
<td>-0.75</td>
<td>0.82</td>
<td>2.22</td>
<td>0.66</td>
<td>+3.4%</td>
</tr>
</tbody>
</table>

was N^d^U + N^σ^U + N^Ir^0 = 9.0, in agreement with Eq. (2). The negative sign of the obtained SHA is opposite to the positive value of +2.1% in experiment [3]. However, the small value of δ_i is consistent with the previous estimation of |δ_i| = 0.1 [7,8]. Motivated by the idea in Fig. 1, we will check the effect of local electron correlation U in the following section.

Quantum Monte Carlo results.—Because of the experimental observation that the SHA of CuIr is independent of the concentration of Ir impurities [3], we employ a single-impurity multiorbital Anderson model with SOI [9,15,16]

\[
H = \sum_{k,\alpha,\sigma} \epsilon_{k\alpha} c_{k\alpha}^\dagger c_{k\alpha} + \sum_{k,\alpha,\xi,\sigma} (V_{\xi k \alpha} d_{\xi\alpha}^\dagger c_{k\alpha} + H.c.) + \sum_{\xi,\sigma} \epsilon_{\xi \sigma} n_{\xi \sigma} + U \sum_{\xi} n_{\xi \uparrow} n_{\xi \downarrow} + U' \sum_{\xi,\sigma,\sigma'} \sum_{\xi} n_{\xi \sigma} n_{\xi \sigma'} - \frac{J}{2} \sum_{\xi,\sigma} n_{\xi \sigma} n_{\xi \sigma\downarrow} + \frac{J}{2} \sum_{\xi,\sigma} \langle \sigma \rangle \langle \sigma \rangle \sum_{\xi} d_{\xi \sigma}^\dagger d_{\xi \sigma},
\]

(11)

where \( c_{k\alpha} \) is the energy band \( \alpha \) of host Cu, \( \epsilon_{\xi \sigma} \) is the energy level of the 5d orbital \( \xi \) of impurity Ir, \( V_{\xi k \alpha} \) is the hybridization between the 5d orbital \( \xi \) of Ir and the band \( \alpha \) of Cu, and \( J \) is the strength of SOI. \( U (U') \) is the on-site Coulomb repulsion within (between) the 5d orbitals of Ir, and \( J \) is Hund coupling between the 5d orbitals of Ir. The \( \epsilon_{k\alpha}, \epsilon_{\xi \sigma}, \) and \( V_{\xi k \alpha} \) can be obtained from the codes of QE [17] and Wannier90 [19], respectively [20].

We apply the quantum Monte Carlo (QMC) method [20–22], which can correctly include the local electron correlations, to calculate the occupation numbers \( n_\sigma \) of 5d orbitals of Ir. The parameters of correlation and SOI of Ir are given to be \( U = 0.5 \) eV and \( \lambda = 0.5 \) eV [23,24]. The relations of \( U = U' + 2J \) and \( J/U = 0.3 \) [25] give \( J = 0.15 \) eV and \( U' = 0.2 \) eV.

In order to allow convergence down to room temperature in a tractable calculation, of the five 5d orbitals of Ir, only the three \( t_{2g} \) orbitals were retained, and only the diagonal component of the SOI is conserved. It is reasonable to neglect the \( e_g \) orbitals because there are no spin-orbit matrix elements. It is convenient to transform the three \( t_{2g} \) orbitals into \( t_{1-1}, t_0, \) and \( t_1; t_{1-1} \equiv -(1/\sqrt{2})(xz - iy_z) = -Y_{2,-1}, \) \( t_0 \equiv -ixy = -(1/\sqrt{2})(Y_{2,-2} - Y_{2,-2}), \) and \( t_1 \equiv -(1/\sqrt{2})(xz + iy_z) = Y_{2,1}, \) which are expressed by spherical harmonics with the orbital angular momentum \( \ell^C = -1, 0, \) and 1 of \( l = 2, \) respectively. The QMC calculation is performed with more than 10^6 Monte Carlo sweeps, the Matsubara time step \( \Delta \tau = 0.25, \) and temperature \( T = 360 \) K.

The QMC calculation [15,16] can give the occupation number \( \langle n_{l-1}, \rangle, \langle n_0 \rangle, \) and \( \langle n_l \rangle \) for each \( t_{2g} \) orbital. The average value of the \( z \) component of the spin-orbit correlation function \( \langle \xi'^C \sigma'^C \rangle = \langle -n_{l-1} + n_{l-1} + n_{l+1} - n_{l+1} \rangle, \) can also be obtained. The occupation numbers of parallel and antiparallel states can be written as \( n_p = \langle n_{l-1} \rangle + \langle n_{l+1} \rangle, \) \( n_{AP} = \langle n_{l-1} \rangle + \langle n_{l+1} \rangle, \) which can be obtained from the relations of \( \langle \xi'^C \sigma'^C \rangle = n_p - n_{AP} \) and \( \langle n_l \rangle = n_p + n_{AP}. \) These occupation numbers are related to the the phase shift of the parallel (antiparallel) state of the \( t_{2g} \) orbitals of Ir as \( \delta_p = \pi n_p/2 (\delta_{AP} = \pi n_{AP}/2). \) We assume that \( \delta_p \) (respectively, \( \delta_{AP} \)) from the simplified model can be taken as the phase shift \( \delta^d_{l\uparrow}, (\delta^d_{l\downarrow}) \) of the full spin-orbit split 5d orbital of Ir.

With correlation \( U = 0.5 \) eV on the 5d states of Ir impurity, the QMC calculation gives \( \delta^d_{l\uparrow} = 1.59 \) and \( \delta^d_{l\downarrow} = 2.30. \) The occupation numbers can be calculated as \( N^d_{l\uparrow} = 0^d_{l\uparrow}/\pi = 3.03 \) and \( N^d_{l\downarrow} = 40^d_{l\downarrow}/\pi = 2.93, \) and the phase shifts of \( \delta^d_{l\uparrow} \) and \( \delta^d_{l\downarrow} \) then obtained by Eq. (3) to be 

\[
-1.45 \text{ and } -0.75, \text{ respectively, as listed in the case of } U = 0.5 \text{ eV in Table I. Comparing the cases with } U = 0.0 \text{ and } 0.5 \text{ eV in Table I, it is clear that the splitting of the phase shifts, } |\delta^d_{l\uparrow} - \delta^d_{l\downarrow} |, \text{ is enlarged from } 0.35 \text{ to } 0.70 \text{ by the correlation } U = 0.5 \text{ eV. Moreover, the occupation number of } 5d \text{ states is } N^d_{l\uparrow} = N^d_{l\uparrow\uparrow} + N^d_{l\downarrow\downarrow} = 5.96, \text{ which is smaller than the } N^d_{l\downarrow} = 7.82 \text{ without } U, \text{ in agreement with the schema in Fig. 1.}

The decreased electron number in 5d states, which is 1.86, will be transferred to the 6s and 6p states of Ir impurity as discussed by Eq. (2). We do not know precisely how many electrons are transferred to the 6s states and how many to the 6p states. As an approximate estimation [26], we fix the ratio \( N^d_{l\uparrow}/N^d_{l\downarrow} = 2.7 \) which is obtained by LDA with \( U = 0. \) This gives the increased \( N^d_{l\uparrow} = 2.22, \) as shown in the case of \( U = 0.5 \) eV in Table I. Since the occupation numbers for pure Cu (\( N^Cu^0_{l\uparrow}, N^Cu^0_{l\downarrow} \) do not change, the data of \( N^Cu^0 = 0.96 \) and \( N^Cu^0 = 9.68 \) obtained from the \( U = 0 \) case are employed for calculating \( \delta_1 \) and SHA for all positive \( U \) in Table I. Finally, positive \( \delta_1 \) of 0.66 and SHA
We note that, for the entire range of $U$ shown in Fig. 2, the nonmagnetic solution is stable following Ref. [9]. This shows that the change of sign and nonmonotonic behavior of the SHA as a function of $U$ are not a result of the projection onto $t_{2g}$ states, but more general.

Discussion.—Since the sign of SHA is sensitive to the sign of $\delta_1$ [Eq. (10)] and the corresponding small change of $N^0_p$ [Eq. (3)], the sign of SHA might be controlled as long as the occupation number of the $6p$ states of the impurity were properly manipulated. For instance, a laser pulse [28] can decrease the occupation number of the impurity by excitation. An improved combination of noble metal hosts and $5d$ metal impurities with a long lifetime of the excited states may be imagined as a means to control the sign of the SHA.

In summary, we reconsider the theory of the spin Hall effect in CuIr alloys by the QMC method, where the local Coulomb correlation $U$ in $5d$ states of Ir impurities is included. Taking $U$ to be $0.5 \text{ eV}$, we obtain a positive SHA, consistent with experiment, in contrast to the negative angle predicted without correlation $U$. Our result reveals the key physics determining the spin Hall effect in CuIr alloys, explaining the positive sign of the SHA in experiment. This may also open up a way to control the sign of the spin Hall effect by manipulating the occupation number of the impurities.

We are very grateful to A. Fert, P. Levy, M. Chshiev, H. X. Yang, Y. Otani, and Y. Niimi for many stimulating discussions. T. Ziman would like to thank the KITP, UCSB for hospitality during the Spintronics Program 2013, with support in part by the National Science Foundation under Grant No. NSF PHY11-25915. The work has been supported by a REIMEI project of JAERI. This work was supported by Grant-in-Aid for Scientific Research from MEXT (Grant No. 24540387, No. 24360036, No. 23340093, No. 25287094, No. 26247063, and No. 26013006), by bilateral program from MEXT, and supported by a REIMEI project of JAERI. This work was carried out on the supercomputers at JAEA.

[6] The minus sign comes from a consistent definition of the SHA, see below, after Eq. [9] and the previous reference.
[26] Because of the fact that the s and p waves of Ir are quite extended compared to the d waves, we assume the same ratio of $N_{Ir}^s/N_{Ir}^p$ in the model with finite U on 5d around 0.5 eV. The sign of SHA with $U = 0.5$ eV is not sensitive to the ratio, which is confirmed by varying the ratio around 2.7% by 50%, from 1.4 to 4.1. For the ratio of 1.4, it gives $N_{Ir}^p = 1.78$ and SHA = $+4.1\%$; for the ratio of 4.1, it gives $N_{Ir}^p = 2.45$ and SHA = $+2.2\%$.