Analysis of the spin Hall effect in CuIr alloys: Combined approach of density functional theory and Hartree-Fock approximation

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I. INTRODUCTION

The spin Hall effect (SHE) converts charge current into spin current, which is crucial for the further development of spintronic devices. The key material parameter in a spin Hall effect is the ratio between the induced spin Hall current and the spin Hall resistivity increases linearly with the impurity concentration, so that the SHE is predominantly attributed to a skew scattering extrinsic contribution. Hence, the nonmagnetic CuIr alloys can be described by a single-impurity multi-orbital Anderson model.

\[
H_{00} = \sum_{k,\alpha,\sigma} \epsilon_{\alpha k} c_{k\alpha\sigma}^\dagger c_{k\alpha\sigma},
\]

\[
H_0 = H_{00} + \sum_{k,\alpha,\beta,\sigma} (V_{\beta\alpha k\sigma} d_{\alpha\sigma}^\dagger c_{k\alpha\sigma} + \text{H.c.}) + \sum_{\beta,\sigma} \epsilon_{\beta n_{\beta\sigma}},
\]

\[
H_{SO} = \frac{\lambda_p}{2} \sum_{\xi,\xi',\sigma,\sigma'} d_{\xi\sigma}^\dagger (1)_{\xi\xi'} (\sigma_{\sigma'} d_{\xi'\sigma'}
\]

\[
+ \frac{\lambda_d}{2} \sum_{\xi,\xi',\sigma,\sigma'} d_{\xi\sigma}^\dagger (1)_{\xi\xi'} (\sigma_{\sigma'} d_{\xi'\sigma'} - J \sum_{\xi,\xi',\sigma,\sigma'} n_{\xi\sigma} n_{\xi'\sigma'} - J \sum_{\xi,\xi',\sigma,\sigma'} n_{\xi\sigma} n_{\xi'\sigma'}},
\]

\[
H = H_0 + H_{SO} + U \sum_\xi n_{\xi\uparrow} n_{\xi\downarrow}
\]

\[
+ \frac{U'}{2} \sum_{\xi \neq \xi',\sigma,\sigma'} n_{\xi\sigma} n_{\xi'\sigma'} - \frac{J}{2} \sum_{\xi \neq \xi',\sigma} n_{\xi\sigma} n_{\xi'\sigma},
\]

where \( \epsilon_{\alpha k} \) is the energy band \( \alpha \) of the host Cu, \( \epsilon_{\beta} \) is the energy level of the orbital \( \beta \) of the impurity Ir, and \( V_{\beta,\alpha}(k) \) is the hybridization between the orbital \( \beta \) of Ir and the band \( \alpha \) of Cu. \( U \) (\( U' \)) is the on-site Coulomb repulsion within (between) the 5d orbitals of Ir, and \( J \) is the Hund coupling between the 5d orbitals of Ir. The relations of \( U = U' + 2J \) and \( J/U = 0.3 \) are kept.

In the present work, by the combined approach of the density functional theory (DFT) and Hartree-Fock (HF) approximation, we calculate the SHA including correlation effects, and find that the local correlation effects of the 5d orbitals of Ir give the sign of SHA consistent with experiment.

II. SKEW SCATTERING

For the CuIr alloys, the spin orbit interactions (SOI) in the 5d orbitals of the Ir impurities induce the extrinsic SHE. It has been observed in experiment that the spin orbit interactions (SOI) in the 5d orbitals of the Ir impurities induce the extrinsic SHE. It has been observed in experiment that the spin orbit interactions (SOI) in the 5d orbitals of the Ir impurities induce the extrinsic SHE. It has been observed in experiment that the spin orbit interactions (SOI) in the 5d orbitals of the Ir impurities induce the extrinsic SHE. It has been observed in experiment that the spin orbit interactions (SOI) in the 5d orbitals of the Ir impurities induce the extrinsic SHE. It has been observed in experiment that the spin orbit interactions (SOI) in the 5d orbitals of the Ir impurities induce the extrinsic SHE. It has been observed in experiment that the spin orbit interactions (SOI) in the 5d orbitals of the Ir impurities induce the extrinsic SHE. It has been observed in experiment that the spin orbit interactions (SOI) in the 5d orbitals of the Ir impurities induce the extrinsic SHE. It has been observed in experiment that the spin orbit interactions (SOI) in the 5d orbitals of the Ir impurities induce the extrinsic SHE. It has been observed in experiment that the spin orbit interactions (SOI) in the 5d orbitals of the Ir impurities induce the extrinsic SHE.
spectively. For the 5d states with SOI of Ir, we have the relations of
\( n_{d^+} = N_{d^+}^T /6 \) and \( n_{d^-} = N_{d^-}^T /4 \), where
\( n_{d^\pm} \) are the occupation number of each of the degenerate
states 5d\( \pm \), and \( N_{d^\pm}^T \) are the total occupation number
of the 5d\( \pm \) states. The values of \( n_{d^\pm} \) will be between
0 and 1. The total occupation number of the 5d states
of Ir \( N_{d^+}^T = N_{d^+}^T + N_{d^-}^T \). Similarly, the SOI splits the p
orbitals into p\( \pm \) states.

Since a net charge cannot exist in metal, the total oc-
cupation numbers of the valence states of 6s, 6p and 5d
of Ir is conserved as
\[
N_{s^+}^r + N_{p^+}^r + N_{d^r} = 9 ,
\]
where the occupation numbers are defined via projections
of the occupied states onto the Wannier states centered
at the Ir sites and extended in the whole supercell.

Following the method of Ref. \[12\] and the definition of
SHA \( \Theta \) in terms of resistivity \( \rho \) \[8\], the SHA of CuIr can be
calculated from the phase shifts \( \delta_1^\pm \) of the \( p^\pm \) and \( \delta_2^\pm \)
of the \( d^\pm \) channels as
\[
\Theta(\delta_1^+, \delta_1^-, \delta_2^+, \delta_2^-) = A/B ,
\]
\[
A = -2[9\sin(\delta_1^+ - \delta_2^+) \sin(\delta_1^+ \sin \delta_2^+]
- 4\sin(\delta_1^+ - \delta_2^-) \sin(\delta_1^+ \sin \delta_2^-)
- 5\sin(\delta_1^- - \delta_2^-) \sin(\delta_1^- \sin \delta_2^-) ,
\]
\[
B = 45\sin^2 \delta_2^- + 30\sin^2 \delta_2^+ + 50\sin^2 \delta_1^+ + 25\sin^2 \delta_1^- + 6\sin^2(2\delta_1^+ - \delta_2^-)
+ 12\sin \delta_1^+ \sin(2\delta_2^+ - \delta_1^-)
+ 14\sin \delta_1^+ \sin(2\delta_2^- - \delta_1^-) - 2\sin \delta_1^- \sin(2\delta_2^- - \delta_1^-) .
\]

The phase shifts can be obtained by the Friedel sum rule
\[1, 10\] :
\[
\delta_\mu^\pm = \pi(N_{\mu^+}^T - N_{\mu^-}^Cu /D_{\mu^\pm} ,
\]
where \( \mu = 1 \) for \( p \) orbitals with the degeneracies
\( D_{1^+} = 4 \) and \( D_{1^-} = 2 , \mu = 2 \) for d orbitals with
\( D_{2^+} = 6 \) and \( D_{2^-} = 4 \).

III. DFT RESULTS

For the DFT calculation, we employ the code of Quan-
tum Espresso (QE) \[12\]. We use a primitive cell of a
single Cu atom to calculate the \( H_{990} \) exclusively for the
case of pure Cu, and a supercell of Cu\(_{26}\)Ir to calculate
the \( H_0 \) for the case of CuIr alloys. The cutoff energy
of planewaves is 50 Ry. The pseudopotentials are ultrasoft
for calculations without SOI and projector-augmented-
wave for calculations with SOI. The type of exchange-
correlation functionals is PBE \[13\] . The energy conver-
gence limit is \( 10^{-3} \) Ry. The \( k \) lattice is \( 8 \times 8 \times 8 \).

By the DFT calculations of \( H_{990} \) and \( H_0 \) in Eq. (1)
for pure Cu and CuIr, respectively, the occupation numbers
of 4s, 4p, 3d states of Cu and 6s, 6p, 5d states of Ir are
obtained to be \( N_{s^+}^Cu = 0.35 , \ N_{p^+}^Cu = 0.96 , \ N_{d^+}^Cu = 9.68 \)
and \( N_{d^+}^r = 0.32 , \ N_{p^+}^r = 0.86 , \ N_{d^+}^r = 7.82 \), respectively. Thus the
total occupation number \( N_{d^+}^T + N_{p^+}^T + N_{d^r} = 9.0 \), confirming
the relation in Eq. (2). Including the SOI, the DFT
calculations for pure Cu and CuIr give the phase shifts of
\( \delta^+ = -0.09 , \delta^- = 0.06 , \delta^+_2 = -0.73 \) and \( \delta^-_2 = -0.38 \), by Eq. (3).

IV. DFT+HF APPROACH

The hybridization between the 5d orbitals of the Ir
impurity and the Cu host is defined as
\[
V_{\xi \kappa \alpha \kappa} \equiv \langle \varphi_\xi | H_0 | \Psi_\alpha (k) \rangle ,
\]
where \( \varphi_\xi \) is the Ir impurity state in real space with the 5d
orbital index \( \xi \), and \( \Psi_\alpha (k) \) is the Cu host state in k-space
with the band index \( \alpha \) and wavevector \( k \). Following the
method in Ref. \[14\], and using the post-processor code
Wannier90 \[15\] , \( V_{\xi \kappa \alpha \kappa} \) were obtained. In Fig. we plot
the overlap of each virtual bound state for each 5d orbital \( \xi \) of
Ir is obtained by the relation \[13\] :
\[
\Delta_\xi = \pi \sum_{\alpha, \kappa} \delta(\epsilon_F - \epsilon_{\alpha \kappa}) |V_{\xi \kappa \alpha \kappa}|^2 ,
\]
where \( \epsilon_F \) is the Fermi level. As a result, the width \( \Delta \)
for the whole 5d orbitals of Ir is the average of each \( \Delta_\xi \),
\( \Delta = \sum_\xi \Delta_\xi /5 = 1.76 \) eV.

Based on the Anderson model \[5\], the 5d states of Ir
impurities are considered as virtual bound states with
width \( \Delta \). Including correlation \( U \) on the virtual bound
states, the impurity level increases while the occupation
number decreases, as shown schematically in Fig. 2. Tak-
ing the results of \( V_{\xi \kappa \alpha \kappa} \) by Eq. (4), the width parameter
\( \Delta_\xi \) of the virtual bound state for each 5d orbital \( \xi \) of
Ir is obtained by the relation \[13\] :
\[
\Delta_\xi = \pi \sum_{\alpha, \kappa} \delta(\epsilon_F - \epsilon_{\alpha \kappa}) |V_{\xi \kappa \alpha \kappa}|^2 ,
\]
where \( \epsilon_F \) is the Fermi level. As a result, the width \( \Delta \)
for the whole 5d orbitals of Ir is the average of each \( \Delta_\xi \),
\( \Delta = \sum_\xi \Delta_\xi /5 = 1.76 \) eV.

Based on the Anderson model of \( H_0 + H_{SO} \) in Eq. (1),
for the nonmagnetic CuIr including SOI but without cor-
relation \( U \), there are self-consistent relations between the
spin-orbit split states of 5d\( + \) and 5d\( - \) of Ir \[5\] :
\[
\Delta \cot (\pi n_{d^\pm}) = E_{0, d^\pm} ,
\]
where the 5d\( \pm \) states of Ir under \( U = 0 \) has the energy level
of \( E_{0, d^\pm} \). The DFT results of \( H_0 + H_{SO} \) in Eq. (1) give

\[\text{FIG. 1. The hybridization function between the 5d orbitals of the Ir impurity and the bulk Cu host.}\]
$n_{d^+} = 0.734$ and $n_{d^-} = 0.849$. Then Eq. (4) gives $E_{0,d^+} = -1.59$ eV and $E_{0,d^-} = -3.43$ eV.

For correlation $U > 0$, based on Eq. (4) with HF approximation, the self-consistent relations are rewritten as

$$E_{d^\pm} = \Delta \cot((\pi n_{d^\pm})$$

$$= E_{0,d^\pm} + U\left(\frac{3}{5}n_{d^+} + \frac{2}{5}n_{d^-}\right) + U'\left(\frac{24}{5}n_{d^+} + \frac{16}{5}n_{d^-}\right) - J\left(\frac{12}{5}n_{d^+} + \frac{8}{5}n_{d^-}\right),$$

(8)

from which the $n_{d^+}$ and $n_{d^-}$ can be obtained for each positive $U$. Eq. (8) directly includes all the five 5d orbitals of Ir, as well as the local correlations, and the calculation is self-consistent.

As $U$ increases from 0, the occupation number $N^{Ir}_{d^+} = 6n_{d^+} + 4n_{d^-}$ decreases, as shown in Fig. 3(a). The phase shifts $\delta_{U}^{\pm}$ obtained by Eq. (8) are plotted in Fig. 3(b). The ratios of $N^{Ir}_{d^+}/N^{Ir}_{d^-} = 2.7$ and $N^{Ir}_{p^+}/N^{Ir}_{p^-} = 1.4$ from DFT with $U = 0$, and the relation in Eq. (9) are taken to evaluate the occupation numbers $N^{Ir}_{p(\xi)}$. The phase shifts $\delta_{\xi}^{\pm}$ obtained from Eq. (4) are shown in Fig. 3(c). Finally, the SHA $\Theta(\delta_{\xi}^{\pm}, \delta_{\xi}, \delta_{\xi}^0)$, calculated from Eq. (4), is shown in Fig. 3(d). In order to compare the contributions from the $p$ and $d$ orbitals separately, we consider the two limiting cases of $\delta_{\xi}^{+} = \delta_{\xi}^{-} = \delta_{\xi}$ and $\delta_{\xi}^{+} = \delta_{\xi}^{-} = \delta_{\xi}^0$. We define $\delta_{\xi}^0$ and $\delta_{\xi}^{0}$ from Eq. (4) with the total occupations of each orbital and the degeneracies 6 and 10 respectively, and plot them in Figs. 3(c) and (b). The SHA of the two limiting cases $\Theta(\delta_{\xi}, \delta_{\xi}, \delta_{\xi})$ and $\Theta(\delta_{\xi}^0, \delta_{\xi}^0, \delta_{\xi}^0)$ are plotted in Figs. 3(d).

In addition, we need to evaluate the range of $U$ within which the nonmagnetic state of CuIr is the ground state. Following Anderson’s method to calculate the critical value of $U$ between nonmagnetic and magnetic states [8], neglecting the SOI as an approximation, based on the $H - H_{SO}$ in Eq. (4), there are self-consistent relations among the five degenerate 5d orbitals:

$$E_{\xi,\sigma} = \Delta \cot(\pi n_{\xi,\sigma})$$

$$= E_0 + U n_{\xi,\sigma} + U' \sum_{\xi' \neq \xi} (n_{\xi',\sigma} + n_{\xi',-\sigma})$$

$$- J \sum_{\xi' \neq \xi} n_{\xi',\sigma},$$

(9)

For the nonmagnetic case, $n_{\xi,\sigma} = n_{\xi,\sigma} = n$, we have

$$\Delta \cot(\pi n) = E_0 + U n + 8U' n - 4J n.$$  (10)

Taking the parameters of $n = 0.78$ obtained from the DFT calculation of $H_0$ in Eq. (11) and $\Delta = 1.76$ eV obtained from Eq. (10), Eq. (11) gives $E_0 = \Delta \cot(\pi n) = -2.16$ eV.

For the magnetic case, by differentiating Eq. (9),

$$- \frac{\Delta}{\sin^2 \pi n} \delta_{\xi,\sigma} = U \delta_{\xi,-\sigma} + U' \sum_{\xi' \neq \xi} (\delta_{\xi',\sigma} + \delta_{\xi',-\sigma})$$

$$- J \sum_{\xi' \neq \xi} \delta_{\xi',\sigma},$$

(11)

Letting $\delta_{n_{\xi}} = \sum_{\xi} \delta_{\xi,\sigma}$, from Eq. (11)

$$- \frac{\Delta}{\sin^2 \pi n} \delta_{n_{\sigma}} = U \delta_{n_{-\sigma}} + U' (4\delta_{n_{\sigma}} + 4\delta_{n_{-\sigma}}) - 4J \delta_{n},$$

(12)

$$\frac{\Delta}{\sin^2 \pi n} (\delta_{n_{\uparrow}} - \delta_{n_{\downarrow}}) = (U + 4J)(\delta_{n_{\uparrow}} - \delta_{n_{\downarrow}}).$$

(13)

For the magnetic case, $\delta_{n_{\uparrow}} - \delta_{n_{\downarrow}} \neq 0$, thus

$$\frac{\Delta}{\sin^2 \pi n} = U + 4J.$$  (14)
With the parameters of $\Delta=1.76$ eV and $E_0=-2.16$ eV already obtained above, and the fixed relations of $U' = U - 2J$ and $J = 0.3U$ [5, 6], by solving Eqs. (10) and (14) simultaneously, it gives the critical occupation number $n_c$ and the critical correlation parameter $U_c$ between the nonmagnetic phase and magnetic phase to be $n_c=0.30$ and $U_c=3.92$ eV. The critical value of the total occupation number $(N_d^f)_c = 10n_c=3.0$. Thus the results in Fig. 3 are of the nonmagnetic states. As the correlation $U$ increases from zero up to the nonmagnetic limit of 3.92 eV, the SHA is non-monotonic.

V. ANALYSIS OF THE SPIN HALL EFFECT

As shown in Fig. 3(a), as the correlation $U$ on the 5$d$ orbitals of Ir increases from 0, $N_d^f$ decreases, which is consistent with the picture from the Anderson model [1] as in Fig. 2. Due to the relation in Eq. (2), the decrease of $N_d^f$ is accompanied by the increase of $N_f^d$. According to Eq. (3), the phase shifts $\delta_1$ and $\delta_2$ increase and $\delta_3$ decrease, while $\delta_1$ and $\delta_3$ increase from negative to positive, and $\delta_2$ is always positive and increases in magnitude, as shown in Fig. 3(b) and (c).

From Fig. 3(d), we note that at $U=0$, the magnitude of the calculated SHA $\Theta(\delta_1, \delta_2, \delta_2)$ with SOI only in the $p$ orbitals is larger than $\Theta(\delta_1, \delta_1)$, with SOI only in the $d$ orbitals. This is consistent with the results in Ref. [10]. As the correlation $U$ increases to a realistic value for Ir of around 0.5 eV [11], the SHA including SOI in both $p$ and $d$ orbitals, $\Theta(\delta_1, \delta_2, \delta_2)$, goes from negative to positive values. At $U=0.5$ eV, the SHA is $+1.6\%$, quite close to the experimental value of +2.1\% [1]. If the SOI is included only in the 5$d$ orbitals of Ir, the resulting SHA $\Theta(\delta_1, \delta_1, \delta_1, \delta_2)$ still qualitatively follows the complete function $\Theta(\delta_1^+, \delta_1^-, \delta_2^+, \delta_2^-)$. If, on the other hand, we consider the SOI only in the $p$ orbitals, the predicted SHA $\Theta(\delta_1^+, \delta_1^-, \delta_2^+, \delta_2^-)$ around $U=0.5$ eV is opposite in sign to the experiment. This is because the relative magnitudes of $\Theta(\delta_1, \delta_1, \delta_2^+, \delta_2^-)$ and $\Theta(\delta_1^+, \delta_1^-, \delta_2, \delta_2)$ are reversed as $U$ increases from 0 to the realistic value. In addition, the SOI of the more extended 6$p$ orbitals of Ir is likely to be overestimated by the DFT calculation; thus the contribution due to the SOI in the $p$ orbitals terms may be exaggerated. These results suggest the physical reason for the SHA of CuIr observed in experiment: it is the local correlation effects of the 5$d$ orbitals of Ir which determine the sign of the SHA.

In conclusion, by the combined approach of DFT and HF approximation, we show that the local correlation effects of the 5$d$ orbitals of Ir give the sign of the SHA consistent with experiment. This indicates it is a convenient and general method to study the influence of local correlations effects on the SHE, for various combinations of hosts and impurities and for a wide range of $U$.

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[1] Y. Niimi, M. Morota, D. H. Wei, C. Deranlot, M. Basletic, A. Hamzic, A. Fert, and Y. Otani, Phys. Rev. Lett. 106, 126601 (2011).
[2] A. Fert, A. Friederich, and A. Hamzic, J. Magn. Magn. Mater. 24, 231 (1981).
[3] A. Fert and P. M. Levy, Phys. Rev. Lett. 106, 157208 (2011); Phys. Rev. Lett. 111, 199904 (2013).
[4] D. V. Fedorov, C. Herschbach, A. Johansson, S. Ostadin, I. Mertig, M. Gradvand, K. Chadova, D. Koderitzch, and H. Ebert, Phys. Rev. B 88, 085116 (2013).
[5] P. W. Anderson, Phys. Rev. 124, 41 (1961).
[6] S. Maekawa, T. Tohyama, S. E. Barnes, S. Ishihara, W. Koshiba and G. Khaliullin, Physics of Transition Metal Oxides, Springer, 2004.
[7] B. Gu, Z. Xu, M. Mori, T. Ziman, and S. Maekawa, arXiv:1402.3012 (unpublished).
[8] Z. Xu, B. Gu, M. Mori, T. Ziman, and S. Maekawa, arXiv:1405.7449 (unpublished).
[9] G. Y. Guo, S. Maekawa, and N. Nagaosa, Phys. Rev. Lett. 102, 036401 (2009).
[10] D. C. Langreth, Phys. Rev. 150, 516 (1966).
[11] A. Johansson, C. Herschbach, D. V. Fedorov, M. Gradhand, and I. Mertig, J. Phys.: Condens. Matter 26, 274207 (2014).
[12] P. Giannozzi et al., http://www.quantum-espresso.org.
[13] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[14] B. Gu, J.-Y. Gan, N. Bulut, G.-Y. Guo, N. Nagaosa, and S. Maekawa, J. Phys. Conf. Ser. 200, 062007 (2010).
[15] A. A. Mostofi et al., Comput. Phys. Commun., 178, 685 (2008).
[16] C. Herschbach, D. V. Fedorov, I. Mertig, M. Gradhand, K. Chadova, H. Ebert, and D. Koderitzch, Phys. Rev. B 88, 205102 (2013).
[17] S. J. Moon, H. Jin, K.W. Kim, W. S. Choi, Y. S. Lee, J. Yu, G. Cao, A. Sumi, H. Funakubo, C. Bernhard, and T.W. Noh, Phys. Rev. Lett. 101, 226402 (2008).