Extrinsic Spin Hall Effect from First Principles

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We present an *ab initio* description of the spin Hall effect in metals. Our approach is based on density functional theory in the framework of a fully relativistic Korringa-Kohn-Rostoker method and the solution of a linearized Boltzmann equation including the scattering-in term (vertex corrections). The skew scattering mechanism at substitutional impurities is considered. Spin-orbit coupling in the host as well as at the impurity atom and the influence of spin-flip processes are fully taken into account. A sign change of the spin Hall effect in Cu and Au hosts is obtained as a function of the impurity atom, and even light elements like Li can cause a strong effect. It is shown that the *gigantic* spin Hall effect in Au can be caused by skew scattering at C and N impurities which are typical contaminations in a vacuum chamber.

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During recent years the spin Hall effect (SHE) has attracted a lot of interest caused by its potential to generate spin currents in nonmagnetic materials. It would allow for spintronic devices without the problem of spin injection from a ferromagnet into a nonmagnet. Besides this technological aspect, the microscopic understanding of the effect is of great interest, since it has the same origin as the anomalous Hall effect (AHE). A proper description of the SHE provides the possibility of an extension of the method to magnetic materials and a treatment of the anomalous Hall effect.

After the first proposal of skew scattering [1,2] and the following detailed discussion of the extrinsic SHE by Dyakonov and Perel [3], a possible experimental setup was suggested by Hirsch [4]. Several mechanisms were found to contribute to the SHE and AHE [5–12]. These were the intrinsic contribution described by the Berry curvature [5,11], and the extrinsic contribution where the side jump mechanism [8,9] and skew scattering [6,7] at defects can be distinguished [10,12]. The intrinsic part of the SHE was already calculated for metallic systems by *ab initio* methods [13]. Whereas the extrinsic part, in particular the skew scattering, will be the subject of this Letter.

The SHE was first demonstrated optically in semiconductors [14], and only later were electrical measurements on metallic devices [15–17] performed. These experiments on Al, Cu, Pt, and Au provide a variety of results which can only partly be explained by the intrinsic mechanism [13,18]. Unfortunately, no reliable information is available about defects in the samples under consideration, which makes a comparison between experiment and theory difficult.

Here the extrinsic mechanism caused by the skew scattering at substitutional impurities is considered. Our calculations give an insight into the microscopic mechanism and we propose another explanation for the *gigantic* SHE observed in Au [17], besides a Kondo resonance at Fe impurities [18].

In the first part of the Letter we introduce the approach based on the Korringa-Kohn-Rostoker method and the solution of the linearized Boltzmann equation. Our main focus is the Boltzmann equation since the band structure calculation was mainly described in Refs. [19,20]. Afterwards, first results of the approach are discussed.

For the description of the transport properties we choose the Boltzmann equation which is well suited to describe dilute alloys and allows for separation of the different microscopic mechanisms contributing to the Hall current. The nonequilibrium distribution function $f^n(\mathbf{k}) = f_0^n(\mathbf{k}) + g^n(\mathbf{k})$ of the considered system is separated into the equilibrium function $f_0^n(\mathbf{k})$ and $g^n(\mathbf{k})$ the responser of the system to the perturbation. These functions depend on the crystal momentum $\mathbf{k}$ and the band index n. According to Kohn and Luttinger [21,22], the Boltzmann equation for a homogeneous system

$$\dot{\mathbf{k}}\,{}^n\nabla_{\mathbf{k}} f_0^n(\mathbf{k}) = \sum_{\mathbf{k}'n'} [P^{n'n}_{\mathbf{k}'\mathbf{k}} g^{n'}(\mathbf{k}') - P^{nn'}_{\mathbf{k}\mathbf{k}'} g^n(\mathbf{k})] \quad (1)$$

is given by the force term (l.h.s.) and the collision term (r.h.s.). A crucial point for the skew scattering mechanism is the fact that in the presence of spin-orbit interaction the microscopic reversibility is not any more valid for the scattering probability ($P^{nn'}_{\mathbf{k}\mathbf{k}'} \neq P^{n'n}_{\mathbf{k}'\mathbf{k}}$), although the systems under consideration are space-inversion invariant ($P^{nn'}_{\mathbf{k}\mathbf{k}'} = P^{nn'}_{-\mathbf{k},-\mathbf{k}'}$) [2]. The electrons are driven by an applied electric field $\dot{\mathbf{k}}^n = -e\mathbf{E}$ ($e > 0$) and the system is forced to a steady state by the collision term. This term is calculated in the dilute limit of impurity concentrations ($c_0 N$—number of impurities) from Fermi's golden rule [20,23]

$$P^{nn'}_{\mathbf{k}\mathbf{k}'} = \frac{2\pi}{\hbar} c_0 N |T^{nn'}_{\mathbf{k}\mathbf{k}'}|^2 \delta(E^n_{\mathbf{k}} - E^{n'}_{\mathbf{k}'}). \quad (2)$$

The transition matrix in the atomic sphere approximation is given by [20]

$$T^{nn'}_{\mathbf{k}\mathbf{k}'} = \sum_j \int_{\Omega^j_{ASA}} d\mathbf{r} \mathring{\Psi}^{n'\dagger}_{\mathbf{k}'}(\mathbf{r}+\mathrm{R}_j)\Delta V_j(r)\Psi^n_{\mathrm{k}}(\mathbf{r}+\mathrm{R}_j). \quad (3)$$

It describes the scattering of Bloch waves (four component spinors) with spin-mixed character resulting from the relativistic treatment of the ideal and perturbed system at a potential perturbation $\Delta V_j(r)$. Here j runs over all atoms of the impurity cluster. The impurity problem for the potential and the perturbed wave functions $\Psi^n_{\mathbf{k}}(\mathbf{r})$ is solved self-consistently on a real space cluster of 55 atoms via Dyson and Lippman-Schwinger equations starting from the unperturbed ideal crystal with the Bloch states $\mathring{\Psi}^n_{\mathbf{k}}(\mathbf{r})$ [23].

Under the approximation of a weak electric field and the knowledge of a Fermi-Dirac distribution in equilibrium, the linearized Boltzmann equation

$$\mathbf{\Lambda}^n(\mathbf{k}) = \tau^n_{\mathbf{k}}\left[\mathbf{v}^n_{\mathbf{k}} + \sum_{\mathbf{k}'n'} P^{n'n}_{\mathbf{k}'\mathbf{k}}\mathbf{\Lambda}^{n'}(\mathbf{k}')\right] \quad (4)$$

is obtained. Here the unknown quantity is the mean free path $\mathbf{\Lambda}^n(\mathbf{k})$ determined by the relaxation time

$$(\tau^n_{\mathbf{k}})^{-1} = \sum_{\mathbf{k}'n'} P^{nn'}_{\mathbf{k}\mathbf{k}'}, \quad (5)$$

the group velocity

$$\mathbf{v}^n_{\mathbf{k}} = \frac{1}{\hbar}\frac{\partial E^n_{\mathbf{k}}}{\partial \mathbf{k}}, \quad (6)$$

and the scattering-in term $\sum_{\mathbf{k}'n'} P^{n'n}_{\mathbf{k}'\mathbf{k}}\mathbf{\Lambda}^{n'}(\mathbf{k}')$ [24,25]. The linearized Boltzmann equation is an integral equation and can be solved iteratively [23,25,26]. In the low temperature limit the conductivity tensor is given by a Fermi surface integral [23]

$$\underline{\sigma} = \frac{e^2}{\hbar}\sum_n \frac{1}{(2\pi)^3}\iint_{E_{\mathbf{k}}=E_F}\frac{dS_n}{|\mathbf{v}^n_{\mathbf{k}}|}\mathbf{v}^n_{\mathbf{k}} \circ \mathbf{\Lambda}^n(\mathbf{k}). \quad (7)$$

For the spin conductivity $\underline{\sigma}^s$, the spin polarization, defined as the expectation value of the spin operator for the states $\Psi_{n\mathbf{k}}$ on the Fermi surface

$$s^n_z(\mathbf{k}) = \langle\Psi_{n\mathbf{k}}|\hat{\beta}\sigma_z|\Psi_{n\mathbf{k}}\rangle, \quad (8)$$

has to be included

$$\underline{\sigma}^s = \frac{e^2}{\hbar}\sum_n \frac{1}{(2\pi)^3}\iint_{E_{\mathbf{k}}=E_F}\frac{dS_n}{|\mathbf{v}^n_{\mathbf{k}}|}s^n_z(\mathbf{k})\mathbf{v}^n_{\mathbf{k}} \circ \mathbf{\Lambda}^n(\mathbf{k}). \quad (9)$$

The conductivities ($\underline{\sigma}$ and $\underline{\sigma}^s$) include the vertex corrections in the dilute limit [27] due to the scattering-in term in Eq. (4). For degenerate bands in a nonmagnetic system with space-inversion symmetry, the procedure introduced in Ref. [19] is applied to put the quantization axis along the z direction for each $\mathbf{k}$ point. This is necessary to simulate a tiny external magnetic field or ferromagnetic leads to align the electron spins. Following Ref. [19], we denote the wave functions with a positive spin expectation value as Ψ^+ and with a negative one as Ψ^- states, respectively.

The quantum mechanical properties of the system, i.e., the result of the *ab initio* calculation, enter the conductivity evaluation threefold. First, the topology of the Fermi surface determines the states contributing to the conductivity. Second, their Fermi velocities $\mathbf{v}^n_{\mathbf{k}}$, defined by Eq. (6), are taken into account. Finally, the collision term in the Boltzmann equation is calculated from the unperturbed $\mathring{\Psi}^n_{\mathbf{k}}(\mathbf{r})$ and the perturbed $\Psi^n_{\mathbf{k}}(\mathbf{r})$ wave functions of a system with substitutional impurities.

From Fermi's golden rule [Eq. (2)] it follows immediately that, in the dilute limit, the conductivity scales inversely with the number of impurities c_0N. Consequently the ratio of spin Hall conductivity σ^s_{yx} and charge conductivity σ_{xx} is independent on the impurity concentration c_0. This ratio

$$\alpha = \frac{\sigma^s_{yx}}{\sigma_{xx}} \quad (10)$$

is called the *Hall angle* [16–18].

All calculations presented below are performed with a $\mathbf{k}$-point mesh larger than 2000 points on a piece of the Fermi surface which lies in the irreducible part of the Brillouin zone. The angular momentum cutoff of $l_{\max} = 3$ is used. A convergence test for these parameters, as well as for the size of the perturbed cluster (55 atoms), turned out that the relative errors of the Hall angle are smaller than 2%.

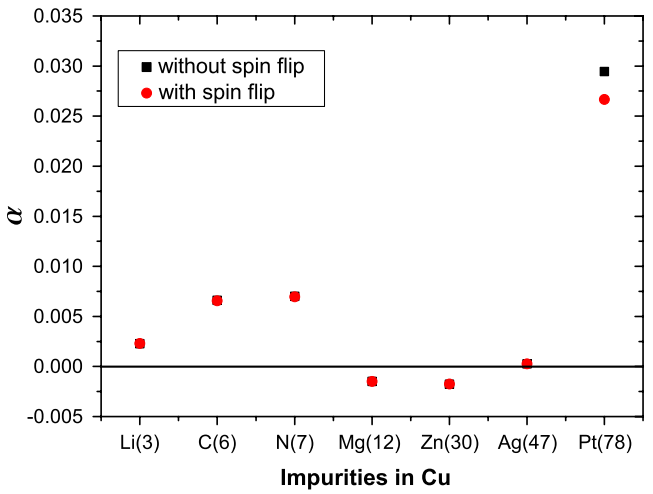

FIG. 1 (color online). The Hall angle α for different substitutional impurities in a Cu host. The number in parentheses gives the core charge connected with the spin-orbit coupling strength at the impurity site.

As the first result, in Fig. 1 the Hall angle α is presented for different substitutional impurities in a Cu host. Without going into details three conclusions can be drawn. First, the very light element Li, which provides nearly no spin-orbit coupling at the impurity site, produces a larger effect than the much heavier element Ag. Second, sign changes of the SHE can occur for some impurities. Finally, the influence of the spin-flip scattering is almost negligible for all impurities.

The presence of a strong extrinsic SHE caused by light impurities is the consequence of the size of the transition matrix elements in Eq. (3). Important for a strong scattering from state $\mathbf{k}$ into $\mathbf{k}'$ is a large potential difference $\Delta V_j(r)$. The spin-orbit coupling is contained in the wave functions already and provided by the host material. Although the spin-orbit interaction caused by Ag is much stronger, the small potential change induced by this isoelectronic element in Cu prevents a sizeable SHE. The mechanism is similar to the effect of the strong spin-flip scattering at light impurities explained in Ref. [20].

The sign change caused by Mg and Zn impurities is more subtle and needs a closer look into the microscopic scattering process included in the Boltzmann equation. As introduced above, the states are separated in Ψ^+ and Ψ^- states by the orientation of their spin polarization along the z axis. The skew scattering process, which is considered here, leads to different scattering amplitudes for these states [6,7,10]. Assuming the incoming state to propagate along the x direction gives an outgoing wave function scattered mainly to the left $(+y)$ or right $(-y)$ depending on the spin state of the wave function. In Fig. 2 the microscopic scattering probabilities for a given state $\mathbf{k}$ are shown as a function of the final states $\mathbf{k}'$ on the Fermi surface of Cu. To visualize the effect of skew scattering, which is usually much weaker than the momentum scattering, the difference $(P^{++}_{\mathbf{k}\mathbf{k}'} - P^{--}_{\mathbf{k}\mathbf{k}'})$ between the probabilities for Ψ^+ and Ψ^- states is shown. The spin-conserving scattering is considered only. The clear asymmetry between the two spin channels is the origin of the spin current and the spatial spin separation, i.e., of the SHE. In addition, the spin separation processes for Zn [Fig. 2(a)] and Li impurities [Fig. 2(b)] are opposite and cause the different sign of the SHE (Fig. 1).

This analysis considers incoming electrons in the x direction only, the spin separation caused by the skew scattering depends strongly on the wave vector $\mathbf{k}$. For the evaluation of the conductivity tensor, all directions of incoming states have to be considered.

Furthermore, we present the SHE for different impurities in a Au host. The idea is to check if the gigantic SHE of $\alpha \sim 0.1$ measured by Seki *et al.* [17] can be understood in the framework of our approach. As discussed already above, there are several requirements to create a system that exhibits a large SHE. First, a host has to provide significantly spin-mixed Bloch functions. Second, either

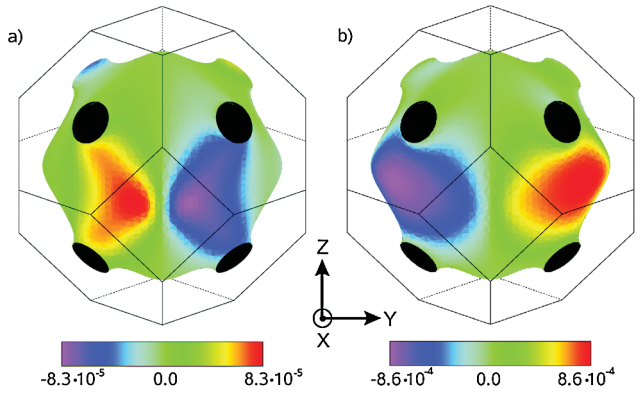

FIG. 2 (color). The skew scattering for (a) Zn and (b) Li impurities in a Cu host. The distribution of $(P^{++}_{\mathbf{k}\mathbf{k}'} - P^{--}_{\mathbf{k}\mathbf{k}'})$ is shown (in arbitrary units) for states $\mathbf{k}'$ at the Fermi level, where the incoming momentum $\mathbf{k}$ points in the [100] direction. The spin polarization for all wave functions is aligned in [001] for Ψ^+ states and in the $[00\bar{1}]$ direction for Ψ^- states, respectively.

the spin-orbit coupling at the impurity site should be strong or the perturbation of the potential has to be large. Consequently, the heavy impurities Ag and Pt are calculated in a Au host. In addition, the light atoms Li, C, and N are considered. The results for α in Au, summarized in Fig. 3, show a very counterintuitive picture. Heavy impurities like Pt and Ag cannot explain the large effect, but typical contaminations in a standard vacuum chamber, like C and N, cause a *gigantic* Hall angle. This result is not in contradiction to the already proposed mechanism originating from a Kondo resonance at Fe impurities, since we are not able to judge which explanation is relevant for the samples investigated in Ref. [17]. Whether the Kondo resonance or the scattering at light impurities causes the *gigantic* spin Hall effect has to be proven experimentally.

In the last part, two important aspects of our calculations are elucidated. Namely, we show how the spin relaxation is included in our calculations. In addition, the importance of the scattering-in term will be discussed. In Cu and Au hosts only two bands are present at the Fermi level with $\Psi^+_{\mathbf{k}}$ and $\Psi^-_{\mathbf{k}}$ degenerate states, according to the spin orientation along the z axis [19]. As a sum over all bands in Eq. (4), we obtain the following expression

$$\mathbf{\Lambda}^+(\mathbf{k}) = \tau^+_{\mathbf{k}}\left[\mathbf{v}^+_{\mathbf{k}} + \sum_{\mathbf{k}'}\{P^{++}_{\mathbf{k}'\mathbf{k}}\mathbf{\Lambda}^+(\mathbf{k}') + P^{-+}_{\mathbf{k}'\mathbf{k}}\mathbf{\Lambda}^-(\mathbf{k}')\}\right] \tag{11}$$

with spin-conserving contributions $P^{++}_{\mathbf{k}'\mathbf{k}}\mathbf{\Lambda}^+(\mathbf{k}')$ and spin-flip contributions $P^{-+}_{\mathbf{k}'\mathbf{k}}\mathbf{\Lambda}^-(\mathbf{k}')$. It turns out that the influence of the spin-flip processes is of minor importance and qualitatively similar results are obtained neglecting the spin-flip contribution (see Figs. 1 and 3).

We show the importance of the scattering-in term using $\underline{\sigma}^s$ in the anisotropic relaxation time approximation. This means that the mean free path of Eq. (4) is taken without

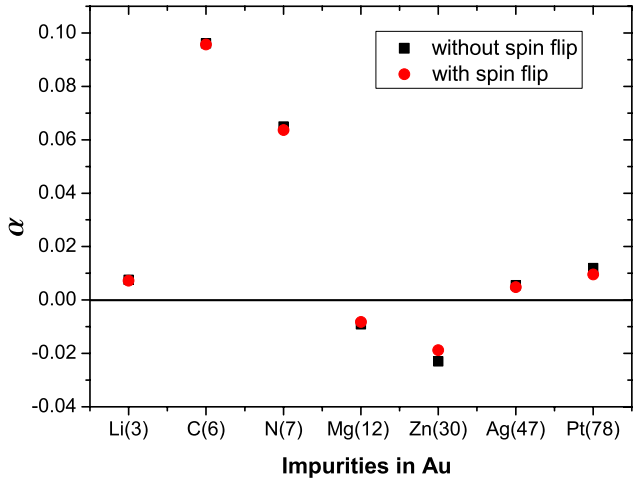

FIG. 3 (color online). The Hall angle α for different substitutional impurities in a Au host.

the scattering-in term: $\mathbf{\Lambda}^n_{(0)}(\mathbf{k}) = \tau^n_{\mathbf{k}} \mathbf{v}^n_{\mathbf{k}}$. Inserting this into Eq. (9) and taking into account that the spins point along the z direction with $s_z^+(\mathbf{k}) = -s_z^-(\mathbf{k}) = |s_z(\mathbf{k})|$, the following expression for the spin conductivity is obtained

$$\sigma_{xy}^{s(0)} = \frac{e^2}{\hbar} \frac{1}{(2\pi)^3} \iint \frac{dS}{|v_{\mathbf{k}}|} |s_z(\mathbf{k})| (\tau^+_{\mathbf{k}} - \tau^-_{\mathbf{k}}) v^x_{\mathbf{k}} v^y_{\mathbf{k}}. \quad (12)$$

From Eq. (12) it is obvious that $\sigma_{xy}^{s(0)} = \sigma_{yx}^{s(0)}$. On the other hand, since the quantization axis is along the z direction and the considered crystals are cubic, C_4 symmetry is present meaning x and y axes are equivalent. So, the symmetry of the system requires an antisymmetric spin conductivity tensor $\sigma_{xy}^{s(0)} = -\sigma_{yx}^{s(0)}$. Thus, both conditions together imply $\sigma_{xy}^{s(0)} = 0$. It shows that the scattering-in term (vertex corrections) is mandatory for the description of the SHE.

In summary, we show that our *ab initio* calculations in combination with the solution of the linearized Boltzmann equation, taking into account the scattering-in term, allow for a description of the skew scattering mechanism in the SHE. The importance of a strong potential perturbation at the impurity site in competition with the strength of the spin-orbit interaction of the substitutional atom is discussed. The sign change of the SHE provided by different impurity atoms in Cu is explained in terms of the microscopic transition probabilities. The extremely large Hall angle induced by C impurities in a Au host is proposed as a possible explanation of the *gigantic* SHE measured in Au. The theoretical results presented here are obtained in the dilute limit of the number of impurities neglecting the intrinsic contribution. For an experimental realization this would mean concentrations of about 1 at. %.

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