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The spin Hall effect in polycrystalline samples of nonmagnetic fifth- and sixth-period metals

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In this paper we propose a method to estimate the coefficient of spin Hall effect for polycrystalline samples of pure nonmagnetic metals. The transverse resistivities characterizing the spin Hall effect were calculated for different metals of the 5th and 6th periods. It is shown that the result within a statistical error agrees with the experimental data.

The spin Hall effect (SHE) consists in the emergence of a measurable transverse spin current [1] under the influence of a charge current in nonmagnetic metals with a strong spin-orbit interaction. The current state of experimental techniques and theoretical research into SHE has been reviewed in detail in several papers (see, e.g., [1–3]). Particular attention has been paid in recent studies to the influence of the structure of epitaxial metal films on spin-dependent transport properties. Specifically, it has been demonstrated that the SHE angle in certain polycrystalline samples increases relative to the corresponding angle in single-crystalline ones [4].

In order to determine the SHE magnitude in a uniform and isotropic polycrystal, we write down the spin-orbit addition to the energy of an electron in an electric field with potential $\Phi(\mathbf{r})$:

$$\hat{V} = -\frac{\hbar e}{2m^2c^2}\varepsilon_{\alpha\beta\gamma}\hat{s}_\alpha\frac{\partial\Phi}{\partial r_\beta}\hat{p}_\gamma. \tag{1}$$

Here, m is the mass of an electron with charge $-e$ and $\varepsilon_{\alpha\beta\gamma}$ is a unit antisymmetric Levi-Civita tensor. The electron momentum dynamics induced by perturbation (1) is characterized by the following equation for averages:

$$\frac{dp_\delta}{dt} = \frac{i}{\hbar}\left\langle\left[\hat{V}, \hat{p}_\delta\right]\right\rangle = \frac{\hbar e \varepsilon_{\alpha\beta\gamma}}{2m^2c^2}\left\langle\hat{s}_\alpha\frac{\partial^2\Phi}{\partial r_\beta\partial r_\delta}\hat{p}_\gamma\right\rangle. \tag{2}$$

The potential of a conduction electron in the crystalline field of ion cores with effective charge Ze and coordinates $\mathbf{R}_k$ is written as $\Phi(\mathbf{r}) = \frac{eZ}{4\pi\varepsilon_0}\sum_{k=1}^{N}\frac{1}{|\mathbf{r}-\mathbf{R}_k|}$.

The value of Z may be estimated by equating the coordinate of the maximum of the radial component of a hydrogen-like wave function to atom radius R_a. For example, platinum has $R_a = 1.39 \cdot 10^{-10}$ m, which corresponds to $Z \approx 22.45$ for shell $6s$. Table 1 lists the properties of atoms of the studied metals, the configurations of their electron shells, and the parameters of their crystal lattices.

In any given spin state of an electron, one may choose such a direction of axis z that the projection of its spin onto this axis assumes a specific value s_z; i.e., $\psi(\mathbf{r}, \sigma) = \psi(\mathbf{r})\delta(\sigma, s_z)$. Let us write the wave function of a collective conduction electron in the form of an expansion in Wannier functions: $\psi(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{n=1}^{N}\Psi(\mathbf{r} - \mathbf{R}_n)\exp(i k\mathbf{R}_n)$, where $\Psi(\mathbf{r})$ is the hydrogen-like function of an electron, $\mathbf{R}_n$ is the translation vector, and N is the number of nodes in a crystallite. Assuming that $\langle\mathbf{s}\rangle = \mathbf{s}$ and substituting variables $\mathbf{r} - \mathbf{R}_k \to \mathbf{r}$, we then obtain the following after summing over spin variables in (2):

$$\frac{dp_\delta}{dt} = \frac{\hbar^2 e^2 Z s_\alpha}{8\pi\varepsilon_0 m^2 c^2 N}\sum_{n,m,k=1}^{N}\exp\left(i\mathbf{k}(\mathbf{R}_n - \mathbf{R}_m)\right)$$

$$\times\left\langle\Psi(\mathbf{r}+\mathbf{R}_k-\mathbf{R}_m)\left|3\frac{r_\delta}{r^5}\hat{l}_\alpha - \frac{\varepsilon_{\alpha\delta\gamma}}{\hbar r^3}\hat{p}_\gamma\right|\Psi(\mathbf{r}+\mathbf{R}_k-\mathbf{R}_n)\right\rangle. \tag{3}$$

Hydrogen-like functions are small at $r > na_\mathrm{B}/Z$, where $a_\mathrm{B} = 5.29 \cdot 10^{-11}$ m is the Bohr radius and n is the principal quantum number. Therefore, the average on the right-hand side of (3) is nonzero only at $\mathbf{R}_n - \mathbf{R}_k = 0$ or $\pm\mathbf{a}_\nu$ and $\mathbf{R}_m - \mathbf{R}_k = 0$ or $\pm\mathbf{a}_\nu$, where $\mathbf{a}_\nu$ is a vector to the nearest neighbor. With the Hermitian nature and odd parity of the operator taken into account, we then obtain

$$\frac{dp_\delta}{dt} = -\frac{\hbar^2 e^2 Z s_\alpha}{4\pi\varepsilon_0 m^2 c^2}\sin(\mathbf{k}\mathbf{a}_\nu)\mathrm{Im}\left\langle\Psi_\nu\left|3\frac{r_\delta}{r^5}\hat{l}_\alpha - \frac{\varepsilon_{\alpha\delta\gamma}}{\hbar r^3}\hat{p}_\gamma\right|\Psi\right\rangle. \tag{4}$$

Here, $\Psi_\nu(\mathbf{r}) = \Psi(\mathbf{r} + \mathbf{a}_\nu) - \Psi(\mathbf{r} - \mathbf{a}_\nu)$ is a function with its parity being opposite to the one of function $\Psi(\mathbf{r})$, and summing over ν is implied.

The right-hand side of relation (4) is equal to the force acting on an electron. It may be presented as the result of influence of Hall electric field $\mathbf{E}_{SH}$ on an electron. Setting $\mathbf{k} = \mathbf{j}mR_H/\hbar$ in (4), where $\mathbf{j}$ is the charge current density,

Table 1. Lattice parameters and electronic configurations of metals of periods 5 and 6

Metal	Lattice structure	Electronic configuration	R_a, pm	Z	b_1	b_2	b_3
Pt	FCC	$5d^9 6s^1$	139	22.45	117	166	204
α-W	BCC	$5d^4 6s^2$	137	22.77	118	136	193
β-W	$A15$	$5d^4 6s^2$	137	22.77	121	187	195
Ta	BCC	$5d^3 6s^2$	149	21	113	131	185
Au	FCC	$5d^{10} 6s^1$	144	21.7	118	167	205
Mo	BCC	$4d^4 5s^1$	139	15.22	78.6	90.4	128
Pd	FCC	$4d^{10} 5s^0$	137	15.4	80.1	113	138
Nb	BCC	$4d^5 5s^1$	146	14.4	78.47	90.49	128

$R_H = 1/(en_e)$ is the Hall constant, and n_e is the density of conduction electrons, we find the following in the first order of smallness in $\mathbf{k}a_\nu$:

$$E_{SH\alpha} = \frac{\hbar Z e R_H s_\beta j_\mu}{4\pi\varepsilon_0 mc^2} a_{\nu\mu} \text{Im} \left\langle \Psi_\nu \left| \frac{\varepsilon_{\alpha\beta\gamma}}{\hbar r^3}\hat{p}_\gamma - 3\frac{r_\alpha}{r^5}\hat{l}_\beta \right| \Psi \right\rangle. \tag{5}$$

Relation (5) is written in the reference frame tied to crystal axes. Let us introduce a laboratory frame tied to the instruments that set the conduction current and measure the spin components. Components of vectors and tensors in the laboratory frame and in the reference frame tied to crystallite axes are denoted by primed indices and indices without prime marks, respectively. Let us convert the vector of the density of current and spin of conduction electrons from the laboratory frame to the frame of crystal axes $j_\mu = p_{\mu\mu'} j_{\mu'}$, $s_\beta = p_{\beta\beta'} s_{\beta'}$ and convert the Hall electric field vector from the frame of crystal axes to the laboratory one $E_{SH\alpha'} = p_{\alpha'\alpha}^{-1} E_{SH\alpha}$, where $p_{\alpha'\alpha}$ is a unit rotation matrix, which is easy to present in terms of Euler angles. We then insert this conversion into Eq. (5) and average vector $\mathbf{E}_{SH}$ in a macroscopic region over random crystallite orientations

$$E_{SH\alpha'} = \frac{\hbar Z e R_H s_{\beta'} j_{\mu'} \overline{p_{\alpha'\alpha}^{-1} p_{\beta\beta'} p_{\mu\mu'}}}{4\pi\varepsilon_0 mc^2}$$

$$\times a_{\nu\mu} \text{Im} \left\langle \Psi_\nu \left| \frac{\varepsilon_{\alpha\beta\gamma}}{\hbar r^3}\hat{p}_\gamma - 3\frac{r_\alpha}{r^5}\hat{l}_\beta \right| \Psi \right\rangle. \tag{6}$$

The overbar denotes averaging over random uniformly distributed Euler angles. Analytical averaging of Eq. (6) yields

$$\mathbf{E}_{SH} = \frac{R_S}{n_e}[\mathbf{j} \times \mathbf{P}],$$

$$R_S = \frac{\hbar R_H e Z}{48\pi\varepsilon_0 mc^2} \text{Re} \left\langle \Psi_\nu \left| \frac{3\mathbf{r}(\mathbf{r}\mathbf{a}_\nu) - \mathbf{a}_\nu r^2}{r^5} \frac{\partial}{\partial \mathbf{r}} \right| \Psi \right\rangle. \tag{7}$$

where $\mathbf{P} = 2sn_e$ is the vector of spin polarization density.

Aligning the polar axis with vector $\mathbf{a}_\nu$, we obtain the following for an s conduction electron for each pair of nearest neighbors:

$$\left\langle \Psi_\nu \left| \frac{3\mathbf{r}(\mathbf{r}\mathbf{a}_\nu) - \mathbf{a}_\nu r^2}{r^5} \frac{\partial}{\partial \mathbf{r}} \right| \Psi \right\rangle$$

$$= \frac{4bZ^3}{a_B^3} \int_0^\infty \frac{dR(x)/dx}{x} dx \int_0^1 y\{R(x_1) - R(x_2)\} dy, \tag{8}$$

where $R(x)$ is the radial part of a wave function, $x = Zr/a_B$, $x_1 = \sqrt{x^2 + b^2 + 2xby}$, $x_2 = \sqrt{x^2 + b^2 - 2xby}$, and $b = Za/a_B$. In the face-centered lattice of platinum, each atom has six pairs of nearest neighbors at distance $a = 2.77 \cdot 10^{-10}$ m, three pairs at a distance of $3.92 \cdot 10^{-10}$ m, and 12 pairs at a distance of $4.48 \cdot 10^{-10}$ m. The following dimensionless parameters, which are used to calculate (8), are then obtained for these three groups of atoms: $b_1 = 117$, $b_2 = 166$, and $b_3 = 204$. These parameters for different metals are also listed in Table 1. It should be noted that the nearest atoms produce the greatest contribution to R_S; the contribution of other atoms is an order of magnitude smaller. Setting $R_H = -2 \cdot 10^{-11}$ m^3/(A $\cdot$ s) for platinum at 80 K, we find $R_S^s = 3.48 \cdot 10^{-9}$ $\Omega \cdot$ m for s electrons. Spin Hall angle $\theta_{SH} = \sigma R_S^e$ [1,3] is normally determined in experiments. Here, σ (often denoted as σ_{xx}) is the conductivity of a metal in the case of zero spin-orbit interaction. In platinum at 10 K, $\sigma = 8.1 \cdot 10^6$ ($\Omega \cdot$ m)$^{-1}$ and $\theta_{SH} = 0.021 \pm 0.005$ [5]. Therefore, $R_S^e = (2.6 \pm 0.7) \cdot 10^{-9}$ $\Omega \cdot$ m.

Theoretical and experimental values of parameter R_S for different metals are listed in Table 2. Tungsten in its metastable β modification has an $A15$ crystal lattice (just as SiCr$_3$). Atoms at the center and corners have six pairs of nearest neighbors at a distance of $2.81 \cdot 10^{-10}$ m, while atoms on the faces have one pair of nearest neighbors at a distance of $2.51 \cdot 10^{-10}$ m. Calculated data reveal that atoms of two sublattices produce equal contributions to SHE.

When formula (8) is used to analyze elements of period 5, the obtained values for s conduction electrons do not agree with experimental ones. At the same time, it is known that conduction bands overlap in transition metals, and a significant fraction of conduction electrons may be produced via collectivization of $5p$ electrons. Apparently,

Table 2. Experimental values of the SHE resistance (R_S^e) and values calculated using formulae (8) and (9) for s (R_S^s) and p electrons (R_S^p)

Metal	σ, 10^5 $(\Omega \cdot m)^{-1}$	θ_{SH},%	Ref.	R_H, 10^{-11} $m^3/(A \cdot s)$	R_S^e, $10^{-9}\,\Omega \cdot m$	R_S^s, 10^{-9} $\Omega \cdot m$	R_S^p, 10^{-9} $\Omega \cdot m$
Pt	81	2.1 ± 0.5	[5]	-2	2.6 ± 0.7	3.48	$-$
Ta	3	-0.37 ± 0.10	[5]	9.75	-13 ± 4	-15.38	$-$
Au	200	0.25 ± 0.05	[6]	-7.3	12 ± 3	7.1	$-$
α-W	47.6	~ -7	[7]	11.1	-14.7	-13.96	$-$
β-W	20.4	-35 ± 4	[8]	-162	$(7.4 \pm 0.8) \cdot 10^2$	$1.66 \cdot 10^3$	$-$
Mo	28	-0.8 ± 0.18	[5]	18	-2.8 ± 0.7	25.4	-4.41
Nb	11	-0.87 ± 0.20	[5]	8.88	-7.9 ± 2.0	10.1	-11.9
Pd	40	0.64 ± 0.10	[9]	-8.45	1.6 ± 0.3	-13.4	1.64

this is especially true for palladium, since it has no $5s$ electrons. Let us align the polar axis for a p conduction electron with vector $\mathbf{a}_\nu$ and measure angle φ from plane $\mathbf{a}_\nu \mathbf{r}$. Unit vector $\mathbf{e}_\varphi$ in spherical coordinates is orthogonal to plane $\mathbf{a}_\nu \mathbf{r}$, and unit vector $\mathbf{e}_\theta$ makes angle $\pi/2 + \theta$ with the polar axis. The normalized wave function of a $5p$ electron oriented along the polar axis takes the form of $\Psi = i\sqrt{3/(4\pi)}R_{5,1}(x)\cos\theta$.

The following is then obtained for each pair of nearest neighbors:

$$\left\langle \Psi_\nu \left| \frac{3\mathbf{r}(\mathbf{ra}_\nu) - \mathbf{a}_\nu r^2}{r^5} \frac{\partial}{\partial \mathbf{r}} \right| \Psi \right\rangle = \frac{3bZ^3}{2\pi a_B^3}$$

$$\times \int_0^\infty \left(\frac{2y\,dR_{5,1}(x)/dx}{x} - \frac{1-y^2}{x^2}R_{5,1}(x) \right) dx$$

$$\times \int_0^1 y\{R_{5,1}(x_1) - R_{5,1}(x_2)\}dy. \qquad (9)$$

The values of SHE resistance calculated using formulae (8) and (9) for metals of period 5 are given in Table 2. A fine agreement with experimental data is obtained if we assume that 95% of conduction electrons in molybdenum are collective p electrons and the remaining 5% are s electrons; in the case of niobium, 85% and 15% of electrons are p and s ones.

The results of theoretical analysis revealed that the spin current does not vanish in the case of a random orientation of crystallites, and calculated data agree with experimental observations. Contributions of the spin-orbit interaction and the band structure of metals to the equivalent electric field are introduced separately into formula (6). The contribution of band structure is expressed using the electron Hall effect constant.

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Conflict of interest

The authors declare that they have no conflict of interest.

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