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Fully relativistic *ab initio* treatment of spin-flip scattering caused by impurities

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We present a fully relativistic approach for the first-principles calculation of the spin-relaxation time of conduction electrons caused by substitutional impurities. It is an extension of our previous nonrelativistic perturbative approach. The approach is based on a relativistic Korringa-Kohn-Rostoker Green's function and band-structure method. As an application, we obtain the spin-flip scattering time for a Cu host with different types of impurities. It is shown that the perturbative approach fails for impurities lighter than the host atoms, while the relativistic treatment provides good agreement with conduction-electron spin-resonance experiments for all considered impurities.

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Spin relaxation becomes an increasingly important problem because of the progress in spintronics.[1–4] Since this process is connected with the spin-orbit interaction, an appropriate relativistic treatment is imperative. In particular, the microscopic understanding of the spin-relaxation anisotropy, which was found to be as large as 20% in graphene,[5] requires a relativistic treatment.

One of the most important spin-relaxation mechanisms is the Elliott-Yafet mechanism.[6,7] For this case, the spin relaxation can be described by a spin-flipping process. It is based on the fact that in the presence of spin-orbit interaction, the spin is not anymore a good quantum number and all electronic states are mixtures of pure "spin-up" and "spin-down" states. As a consequence, impurities, grain boundaries, interfaces, and phonons cause spin-flip scattering processes in addition to the usual momentum scattering.[6–8] Spin-flip scattering can also be initiated by the spin-orbit interaction of impurities and by the phonon-modulated spin-orbit interaction of the lattice ions.[8,9]

In our recent paper,[10] we have shown that in certain situations spin-flip scattering caused by impurities can be properly described using the spin-flip transition matrix calculated in the Born approximation. The spin-orbit interaction was taken into account as an additional perturbation at the impurity site only. This approach is valid if spin-orbit interaction in the host material is negligible in comparison to the spin-orbit interaction at the impurity site.

In this Rapid Communication we present a fully relativistic treatment of the Elliott-Yafet mechanism based on the self-consistent solution of the Kohn-Sham-Dirac equation for the host as well as for the impurity problem. In other words, we extend our previous method for the calculation of the spin-flip scattering time[10] to the fully relativistic case. The main point of interest is how to define spin-flip scattering since the spin is not anymore a conserved quantity. The relativistic spin operator $\hat{\beta}\vec{\sigma}$ does not commute with the Hamiltonian $\hat{H}(\mathbf{r})$ of the Kohn-Sham-Dirac equation (we restrict our consideration to a nonmagnetic system),

$$\hat{H}(\mathbf{r})\Psi_n(\mathbf{r}) = \left[\frac{\hbar}{i}c\hat{\vec{\alpha}}\cdot\vec{\nabla}_{\mathbf{r}} + \hat{\beta}mc^2 + I_4 V(\mathbf{r})\right]\Psi_n(\mathbf{r}). \quad (1)$$

For the solution of Eq. (1), the relativistic Korringa-Kohn-Rostoker method[11–15] is applied.[16] We use spherical potentials in the atomic sphere approximation (ASA),

$$V(\mathbf{r}) = \sum_j V_j(|\mathbf{r}-\mathbf{R}_j|), \quad \text{with } |\mathbf{r}-\mathbf{R}_j| \le R^j_{ASA}. \quad (2)$$

Then the eigenfunctions of $\hat{H}(\mathbf{r})$ inside the jth ASA sphere can be written (for the case of a system with translational symmetry) in the following form:[17]

$$\Psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}_j) = \sum_{\kappa\mu} a^{n,j}_{\kappa\mu}(\mathbf{k})\begin{pmatrix} g^j_\kappa(r)\chi_{\kappa\mu}(\hat{\mathbf{r}}) \\ if^j_\kappa(r)\chi_{-\kappa\mu}(\hat{\mathbf{r}}) \end{pmatrix}, \quad (3)$$

where $a^{n,j}_{\kappa\mu}(\mathbf{k})$ are the expansion coefficients given for each band n and momentum $\mathbf{k}$ and the functions $g^j_\kappa(r)$ and $f^j_\kappa(r)$ are the so-called "large" and "small" components, respectively. In addition, $\chi_{\kappa\mu}(\hat{\mathbf{r}})$ denotes the relativistic spinor functions.[17,18] The corresponding electron eigenvalues are $W_n(\mathbf{k})=E_n(\mathbf{k})+mc^2$, where $E_n(\mathbf{k})$ can be related to the nonrelativistic energy spectrum. All the wave functions given by Eq. (3) have a spin-mixed character, and one cannot use the language of the nonrelativistic treatment with well-defined spin-up and -down states anymore.

Let us consider the case of a nonmagnetic system with space-inversion symmetry. For each pair of degenerate states[6] we can apply the transformation described in Ref. 16 to get two new states $\Psi^+_{n\mathbf{k}}(\mathbf{r})$ and $\Psi^-_{n\mathbf{k}}(\mathbf{r})$ with the spin polarization along a chosen quantization axis. Let us fix the quantization axis along the z direction. Then the superposition of the two original states has to fulfill the condition of zero expectation value for the operators $\hat{\beta}\sigma_x$ and $\hat{\beta}\sigma_y$. In combination with the orthonormalization condition the unitary transformation is defined uniquely at every $\mathbf{k}$ point. Then, the spin polarization is defined as

$$P_{n\mathbf{k}} = \langle\Psi^+_{n\mathbf{k}}|\hat{\beta}\sigma_z|\Psi^+_{n\mathbf{k}}\rangle = -\langle\Psi^-_{n\mathbf{k}}|\hat{\beta}\sigma_z|\Psi^-_{n\mathbf{k}}\rangle. \quad (4)$$

In fact, it is a generalization of the procedure used in Ref. 19 to the case of the Dirac bispinor wave functions. Using such a definition of "+" and "−" states, we can introduce the relativistic spin-relaxation time T^k_1 as (k is a shorthand notation for $\mathbf{k}$ and n)

$$\frac{1}{T_1^k} = \frac{1}{\tau_k^{+-}} + \frac{1}{\tau_k^{-+}} = \sum_{k'} (P^{+-}_{kk'} + P^{-+}_{kk'}). \tag{5}$$

In the equation above, the spin-flip scattering times τ_k^{+-} and τ_k^{-+} are connected with the corresponding transition probabilities $P^{+-}_{kk'}$ and $P^{-+}_{kk'}$. They are calculated by Fermi's golden rule. For instance, the microscopic probability for a transition from a + state k into a − state k' is given by

$$P^{+-}_{kk'} = 2\pi c_0 N |T^{+-}_{kk'}|^2 \delta(E_k - E_{k'}). \tag{6}$$

Here and further on we use Rydberg atomic units. The linear dependence of $P^{+-}_{kk'}$ on the number of impurities c_0N (where c_0 is the impurity concentration and N is the number of atoms in the system) holds for dilute alloys. It is based on the assumption of noninteracting impurities. The corresponding spin-flip transition matrix $T^{+-}_{kk'}$ has to be calculated from the change in the potential $\Delta V(\mathbf{r})$ in the disturbed region around the impurity atom,[20,21]

$$T^{+-}_{kk'} = \sum_j \int_{\Omega^j_{ASA}} d\mathbf{r}\, \mathring{\Psi}^{-\dagger}_{k'}(\mathbf{r}+\mathbf{R}_j)\Delta V_j(r)\Psi^{+}_{k}(\mathbf{r}+\mathbf{R}_j). \tag{7}$$

Here, the bispinor functions $\mathring{\Psi}^{-}_{k'}$ and Ψ^{+}_{k} are unperturbed and perturbed wave functions, respectively. The disturbed region, where charge relaxation is allowed, is restricted in our calculations to a cluster of 55 atoms that corresponds to four nearest-neighbor shells around the substitutional impurity. Using Eq. (3), this expression simplifies to

$$T^{+-}_{kk'} = \sum_j \sum_{\kappa\mu} [\mathring{a}^{-,j}_{\kappa\mu}(k')]^* \Delta^j_\kappa a^{+,j}_{\kappa\mu}(k), \tag{8}$$

where Δ^j_κ is given by

$$\Delta^j_\kappa = \int_0^{R^j_{ASA}} dr\, r^2[\mathring{g}^{j*}_\kappa(r) g^j_\kappa(r) + \mathring{f}^{j*}_\kappa(r) f^j_\kappa(r)]\Delta V_j(r). \tag{9}$$

The averaged value over the Fermi surface is calculated via $1/T_1 = \langle 1/T_1^k \rangle_{E_k=E_F}$.[21,22]

Actually, choosing the quantization axis in other directions (for instance, along ⟨111⟩ instead of ⟨001⟩ direction) should provide for T_1 different results. This effect is caused by the interaction between the spin and the lattice. Generally, a detailed analysis of the anisotropy of the spin-relaxation time with respect to the orientation of the quantization axis is very desirable. Here, we do not concentrate on this point since we expect that the effect should be small for a Cu host.

The most important advantage of our relativistic approach is the consideration of the spin-orbit interaction of the host material. For comparison a method without this influence is introduced in addition. As it was discussed in our previous paper,[10] the spin-relaxation time is related to the spin-flip scattering cross section $\sigma_{\text{sf}} = \Omega_{\text{ws}}/v_{\text{F}} 2T_1 c_0$, where Ω_{ws} is the volume of the Wigner-Seitz cell and v_F denotes the Fermi velocity. Within a spherical band approximation, the scattering cross section can be expressed in terms of differences of the phase shifts δ_j for the levels $j = l \pm 1/2$ of an impurity,[23,24]

$$\sigma_{\text{sf}} = \frac{2}{3}\frac{4\pi}{E_{\text{F}}} \sum_{l>0} \frac{l(l+1)}{2l+1} \sin^2[\delta_{l+1/2}(E_{\text{F}}) - \delta_{l-1/2}(E_{\text{F}})]. \tag{10}$$

Here, the relativistic phase shifts at the impurity site are used but the spin-orbit coupling of the host is neglected.

TABLE I. Spin-relaxation time T_1 in bulk Cu with an impurity concentration of 1 at. %. The experimental results for T_1 were derived from the data for the linewidth of the CESR signal ΔH in Tables III and IV of Ref. 25. The results of the nonrelativistic approach are from Ref. 10. All values are given in ps.

	CESR[a]	Perturbative approach[b]	Our results (relativistic) From Eq. (5)	From Eq. (10)
Impurity	T_1	T_1	T_1	T_1
Li	44 ± 10	2.8×10^7	19	3.2×10^7
Ti	4.2 ± 0.5	18	2.8	9.1
Ni	2.2 ± 0.2	1.6	3.2	3.9
Zn	64 ± 9	49	31	41
Ga	30 ± 4	22	16	16
Ge	14 ± 2	10	9.6	7.1
As	8.6 ± 0.7	5.7	5.4	4.6
Au	0.62 ± 0.21	0.56	0.47	0.38

[a] Reference 25.

[b] Reference 10.

Table I shows the spin-relaxation time T_1 for different impurities in a Cu host calculated using Eq. (5) as well as Eq. (10) in comparison to conduction-electron spin-resonance (CESR) experiments.[25] For all impurities we have a reasonable agreement with experimental data. For the heavier impurities — Ni, Zn, Ga, Ge, As, and Au — our previous nonrelativistic perturbative approach[10] works also well. For impurities with a weaker spin-orbit interaction in comparison to a Cu host (Li and Ti), the fully relativistic description is mandatory to describe the spin-relaxation process properly. The reason is that in our previous method we neglected the spin-orbit coupling in the host, which becomes increasingly important when the impurity atom is lighter in comparison to the host material. In the present approach, the spin-orbit coupling of the host as well as of the impurities is completely taken into account via the relativistic wave functions.

The values of T_1 obtained using Eq. (10) mostly reproduce the results of the perturbative approach and the experimental situation. However, for Li the spin-relaxation time calculated from the phase shifts cannot describe the experimental data. This is evident since the phase shifts account for the spin-orbit coupling at the impurity site only. The atomic number of Li is small and the spin-orbit coupling is negligible. A spin-flip process is only possible if the incoming wave function is already a superposition of spin-up and

-down states. A relatively light impurity, like Li, acts just asa momentum scattering center. The spin relaxation is only provided by the mixed spin character of the Bloch wave function.[6]

This can be seen from the structure of the transition matrix in Eq. (7). The perturbation is just given by the difference of the potential. The action of spin-orbit coupling is hidden in the superposition of spin states of the unperturbed and perturbed wave functions. If the impurity atom is quite light, the spin mixing of the perturbed and unperturbed wave functions is comparable and determined by the spin-orbit coupling of the host material.

It is obvious for Li. For Ti in Cu we have an intermediate situation where both atoms have comparable spin-orbit coupling strengths. In such a case, both contributions, from the host and the impurity site, are important. For all other considered elements the spin-orbit interaction of the impurity atom dominates the relaxation process. It is evident from a comparison to the results calculated using Eq. (10).

Another way of visualizing the influence of unperturbed and perturbed wave functions is to discuss the anisotropic distribution of T_1^k over the Fermi surface shown in Fig. 1. As mentioned in Ref. 10, Ga is mainly a p scatterer, and Ni is mainly a d scatterer. Here, Li is comparable to Zn, which is mainly an s scatterer.[10] This can be seen from the left column of Fig. 1, where the momentum relaxation time is shown. The largest τ_k values are obtained for states k where the corresponding s, p, or d angular momentum character of the host wave function is small.[10,26]

The right-hand side of Fig. 1 shows the spin-relaxation time T_1^k. General features of the distributions over the Fermi surface are similar for all impurities considered, although the absolute values differ substantially. This result is different from the one obtained by the treatment of the spin-orbit coupling as a perturbation at the impurity site only.[10] Under the previous approximation, Zn (s scatterer) and Ga (p scatterer) had similar distributions over the Fermi surface, but Ni (d scatterer) behaved completely different. This was due to the fact that s electrons are not affected by the spin-orbit interaction and for both, Zn and Ga, impurities only p electrons were scattered. The distributions of T_1^k were only determined by the orbital character of the electrons in a Cu host and the impurity atom.[10] Here, we have taken into account the spin-mixed character of the unperturbed wave functions, which is visible in the distribution of the spin-relaxation time. The purple regions with small values of the spin-relaxation time mean strong scattering and coincide with regions of strong spin mixing in Cu.[16] The green, yellow, and red regions are related to the wave functions with small spin mixing and correspondingly weak spin-flip scattering.

In addition, the angular momentum character of the wave functions in a Cu host is important to understand the red regions in the distributions of the spin-relaxation time. For Ga and Li, which are p scatterers, since s states do not contribute to the spin relaxation, the red areas are related to the minimal p character of the electronic states in Cu.[10,26] For Ni impurities the red circles are due to small d character of the electronic states in the host.

In summary, we present a fully relativistic *ab initio* approach for investigations of the spin relaxation caused by substitutional defects. The results obtained for a Cu host are in good agreement with CESR experiments. In particular, they demonstrate that a fully relativistic treatment is needed for a proper description of spin-flip scattering caused by light impurities with a weak spin-orbit interaction in comparison to the host. We discuss the different contributions of unperturbed and perturbed wave functions to the spin-relaxation time for light as well as heavy impurities. For defects such as Ni, Au, and Zn, the spin-orbit coupling in a Cu host could be neglected, but for Li it is essential to describe the situation properly. In addition, we discuss the anisotropic distribution of the scattering times over the Fermi surface of Cu. We

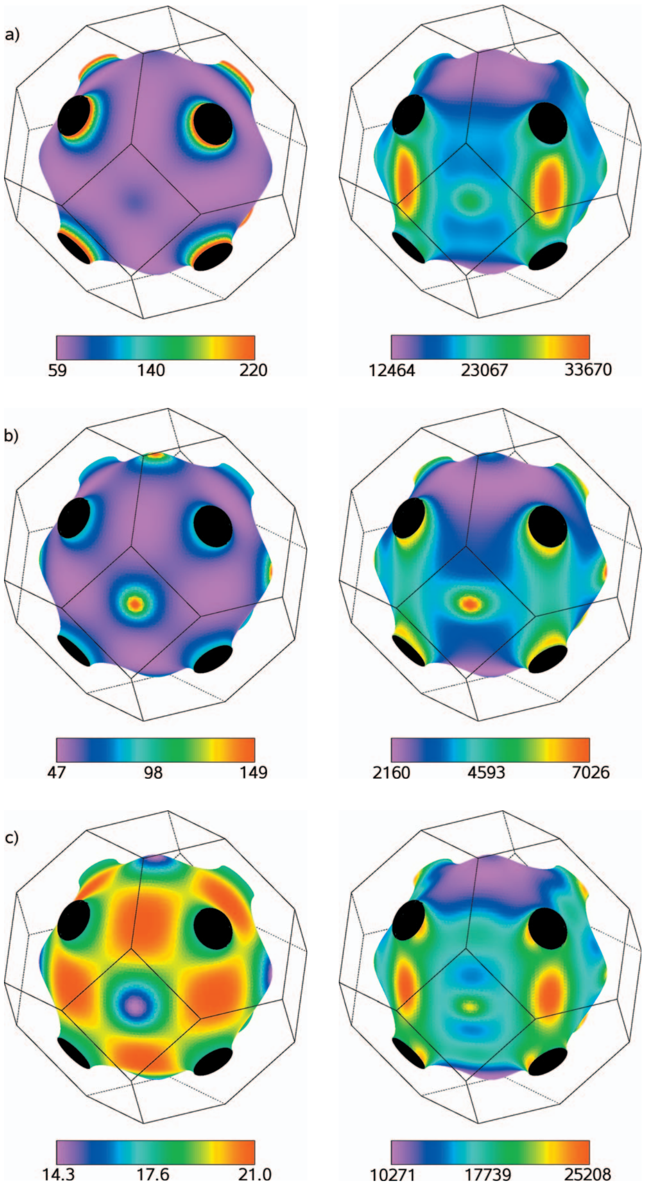

FIG. 1. (Color) Anisotropic $\tau_k=2(1/\tau_k^{++}+1/\tau_k^{--})^{-1}$ (left) and T_1^k (right) on the Fermi surface of Cu for (a) Li, (b) Ni, and (c) Ga impurities with a defect concentration of 1 at. %. All results are given in fs.

show that all main features can be explained by the orbital and the spin-mixing characters of the wave functions in a Cu host in combination with the orbital angular momentum character of the impurity atom. The method presented in this Rapid Communication can be applied for a theoretical study of the Elliott-Yafet spin-relaxation mechanism caused by impurities in all nonmagnetic materials with space-inversion symmetry.

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