PHYSICAL REVIEW B **77**, 092406 (2008)

First-principles calculations of spin relaxation times of conduction electrons in Cu with nonmagnetic impurities

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(Received 15 January 2008; published 13 March 2008)

We have performed *ab initio* calculations of the spin relaxation time of conduction electrons in Cu containing different types of substitutional non-magnetic impurities. The results obtained with the treatment of the spin-flip transition matrix in the Born approximation are in good agreement with conduction electron spin resonance experiments. The distribution of the spin relaxation time over the Fermi surface is strongly related to the electronic properties of the impurity atom. The important role of charge relaxation around the impurity is discussed.

DOI: 10.1103/PhysRevB.77.092406 PACS number(s): 71.70.Ej, 72.25.Rb, 76.30.−v, 85.75.−d

Spintronics is a rapidly emerging field that exploits the spin degree of freedom of the electrons to store, transfer, and process information.[1–4] In this respect, it is highly desirable to know how long the electron spin can be conserved without significant changes. To answer this question, one may use either the spin relaxation time measuring the temporal distance of two scattering events or the spin diffusion length characterizing the spatial separation of two spin-flip events. Recent spintronics experiments[5–7] are able to estimate the spin diffusion length because this quantity is closely related to the spatial distribution of observables. However, the critical point for a theoretical prediction of the spin diffusion length is the calculation of the spin relaxation time.[8,9] Moreover, the latter can also be determined experimentally. For instance, in the first observation of the spin Hall effect,[10] the spin relaxation time was estimated by the decay of the Kerr signal in an external magnetic field. As discussed in Ref. 11, the characteristic behavior of the spin relaxation time observed experimentally points to the dominant role of the Elliott–Yafet[12,13] spin-flip scattering mechanism in metals. In this Brief Report, we examine this spin relaxation mechanism caused by the spin-orbit interaction at the impurity site, and we restrict our considerations to bulk Cu at zero temperature. The considered processes are particularly important for the understanding of the *extrinsic* spin Hall effect.[14–16]

Originally, the spin or magnetization relaxation time was introduced by Bloch[17] to describe the relaxation of magnetization in nuclear magnetic resonance experiments. Dyson[18] gave a definition of the spin relaxation time in the case of conduction electrons. Since the discovery of conduction electron spin resonance (CESR),[19] such experiments were widely used to determine the spin relaxation time in metals. The full width at half amplitude of the absorption resonance with respect to the magnetic field ΔH shows a linear increase with impurity concentration.[20] The spin relaxation time T_1, characterizing the finite lifetime of the spin state, is directly related to the linewidth of the CESR signal by $\Delta H = 2/\gamma T_1$.[20] Here, γ is the gyromagnetic factor.

Our present work is based on the determination of the spin-flip scattering time by means of the probability of a transition between electronic states with opposite spin orientations.[21,22] The spin-flip scattering cross section related to this time will be compared to the results of a simple model based on the scattering phase shift approach.[23,24] A very good agreement with experimental CESR data is obtained. The shortcomings of a non-self-consistent treatment of the impurity problem are discussed.

The electronic structure of bulk Cu was self-consistently calculated in the framework of the nonrelativistic screened Korringa–Kohn–Rostoker multiple scattering Green's function method.[25–27] Spherical potentials in the atomic sphere approximation (ASA) were used. Exchange and correlation effects were included within the local-density approximation in the parametrization of Vosko *et al.*[28] The impurity problem was self-consistently solved in real space on a cluster of 55 atoms, including four nearest neighbor shells around the substitutional impurity to account for charge relaxation.

In the case of a non-magnetic system, the spin relaxation time T_1 is connected with the spin-flip scattering time $\tau^{\mathrm{sf}} = \tau^{\uparrow\downarrow} = \tau^{\downarrow\uparrow}$ by using the relation $T_1 = (1/\tau^{\uparrow\downarrow} + 1/\tau^{\downarrow\uparrow})^{-1} = \tau^{\mathrm{sf}}/2$.[9] The k-dependent spin-flip scattering time τ_k^{sf} (where k is a shorthand notation for the Bloch wave vector $\mathbf{k}$ and band index n)

$$\frac{1}{\tau_k^{\mathrm{sf}}} = \frac{1}{\tau_k^{\uparrow\downarrow}} = \sum_{k'} P_{kk'}^{\uparrow\downarrow} \tag{1}$$

can be calculated by applying Fermi's golden rule

$$P_{kk'}^{\uparrow\downarrow} = 2\pi c_0 N |T_{kk'}^{\uparrow\downarrow}|^2 \delta(E_k - E_{k'}). \tag{2}$$

Here, c_0 is the concentration of impurities and $c_0 N$ is the number of impurity atoms in the system. The linear dependence on the concentration holds for the case of dilute alloys and is based on the assumption that the impurity atoms are noninteracting. The elastic scattering probability $P_{kk'}^{\uparrow\downarrow}$ of the transition of an electron from the "spin-up" state $|\Phi_k^{\uparrow}\rangle$ into the "spin-down" state $|\Phi_{k'}^{\downarrow}\rangle$ is determined by the spin-flip transition matrix for one defect,

$$T_{kk'}^{\uparrow\downarrow} = \int_{\Omega_{\mathrm{ASA}}^{\mathrm{imp}}} d\mathbf{r}\ \Phi_k^{\uparrow\dagger}(\mathbf{r}) \left[\frac{2}{c^2 r} \frac{dV(r)}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \right] \Phi_{k'}^{\downarrow}(\mathbf{r}). \tag{3}$$

The integration is performed over the impurity ASA sphere. In this Brief Report, Rydberg units are used with the speed of light $c=274.074$. The nonrelativistic spinors $\Phi_k^{\uparrow}(\mathbf{r})$ and $\Phi_{k'}^{\downarrow}(\mathbf{r})$ are the perturbed Bloch waves of the dilute alloy related to the corresponding Bloch functions of the ideal host by a Lippmann–Schwinger equation.[29] For a non-magnetic system, they are

$$\Phi_k^{\uparrow}(\mathbf{r}) = \Phi_k(\mathbf{r}) \times \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \Phi_{k'}^{\downarrow}(\mathbf{r}) = \Phi_{k'}(\mathbf{r}) \times \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Thus, Eq. (3) is a Born approximation for the spin-flip transition matrix where the nonvanishing contributions are given by the $\hat{L}_-\hat{S}_+$ component only by applying the expansion of $\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}=(\hat{L}_+\hat{S}_-+\hat{L}_-\hat{S}_+)/2+\hat{L}_z\hat{S}_z$.

With the usual angular momentum expansion of the wave function in the case of spherical atomic potentials,

$$\Phi_k(\mathbf{r}) = \sum_{lm} C_{lm}(k) R_l(r) Y_{lm}(\hat{\mathbf{r}}), \tag{4}$$

we can write

$$\begin{aligned}\frac{1}{\tau_k^{\mathrm{sf}}} = \frac{2\pi c_0}{\Omega_{\mathrm{BZ}}} \sum_{lm} \sum_{l'm'} \xi_l \xi_{l'} C_{lm}^*(k) C_{l'm'}(k) \\ \times \sqrt{l(l+1)-m(m+1)}\sqrt{l'(l'+1)-m'(m'+1)} \\ \times \oint_{E_{k'}=E_F} \frac{dS_{k'}}{|\mathbf{v}_{k'}|} C_{l,m+1}(k') C_{l',m'+1}^*(k').\end{aligned} \tag{5}$$

Here, Ω_{BZ} is the volume of the Brillouin zone and $\mathbf{v}_k$ denotes the group velocity vector of state k at the Fermi level E_F. The functions $Y_{lm}(\hat{\mathbf{r}})$ are the complex spherical harmonics, and the coefficients ξ_l are given by the following expression:

$$\xi_l = \int_0^{R_{\mathrm{ASA}}^{\mathrm{imp}}} dr |R_l(r)|^2 \frac{r}{c^2} \frac{dV(r)}{dr}, \tag{6}$$

where the radial functions $R_l(r)$ are normalized to unity: $\int dr r^2 |R_l(r)|^2 = 1$. Thus, ξ_l corresponds to half of the spin-orbit constants introduced in Ref. 13. To compare with the experiment, we use the spin-flip scattering time averaged over the Fermi surface by using the following procedure:[21,22] $1/\tau^{\mathrm{sf}} = \langle 1/\tau_k^{\mathrm{sf}} \rangle_k$. This average can be related to the spin-flip scattering cross section[20]

$$\sigma_{\mathrm{sf}} = \Omega_{\mathrm{ws}}/v_F \tau^{\mathrm{sf}} c_0, \tag{7}$$

where v_F is the Fermi surface average of the Fermi velocity and Ω_{ws} denotes the volume of the bulk Wigner–Seitz cell, which gives the inverse density of atoms in the host.

The spin-flip scattering cross section σ_{sf} can also be expressed in terms of differences of the phase shifts δ_j for the levels $j=l\pm 1/2$,[23,24]

$$\sigma_{\mathrm{sf}} = \frac{2}{3} \frac{4\pi}{E_F} \sum_{l>0} \frac{l(l+1)}{2l+1} \sin^2[\delta_{l+1/2}(E_F) - \delta_{l-1/2}(E_F)]. \tag{8}$$

Let us now assume a weak scattering and replace the sine in Eq. (8) by the difference of the phase shifts. To first order in the spin-orbit interaction, it can be written as[23] $\delta_{l+1/2}(E_F) - \delta_{l-1/2}(E_F) \approx \pi n_l(E_F)\xi_l/2$, where $n_l(E_F)$ is the angular momentum resolved impurity local density of states at the Fermi level. As a result, we obtain

$$\sigma_{\mathrm{sf}} = \sum_{l>0} \sigma_{\mathrm{sf}}(l) = \frac{2}{3} \frac{\pi^3}{E_F} \sum_{l>0} \frac{l(l+1)}{2l+1} \xi_l^2 n_l^2(E_F). \tag{9}$$

TABLE I. Spin relaxation time T_1 and momentum relaxation time τ in bulk Cu with an impurity concentration of 1 at. %. The experimental results for T_1 were derived from the data for ΔH of Tables III and IV of Ref. 20. For the calculation of τ, the scheme described in Ref. 29 was applied. All values are given in picoseconds.

Impurity	Other calculation[a] T_1	CESR[b] T_1	Our results T_1	Our results τ
Ni	4.0	2.2 ± 0.2	1.9	0.057
Zn	125	64 ± 9	58	0.078
Ga	33	30 ± 4	26	0.017
Ge	14	14 ± 2	12	0.0072
As		8.6 ± 0.7	6.7	0.0043
Au	2.0 ± 0.4	0.62 ± 0.21	0.67	0.48

[a] Reference 22.
[b] Reference 20.

Similar approximations were made in Ref. 24, and it was demonstrated that a good agreement with experiment can be reached for a Mg host.[30] Equation (9) provides a possibility for a simplified analysis of the results discussed below.

Table I summarizes the spin relaxation time T_1 for bulk Cu with different types of impurities calculated by our *ab initio* method. Our calculation is compared with CESR experiments of Monod and Schultz[20] and with the calculation of Holzwarth and Lee.[22] A good agreement between our results and the experimental data is found. The values obtained in Ref. 22 show a significant deviation from the experimental data, except in the case of Ga and Ge impurities. Holzwarth and Lee[22] neglected spin-orbit interactions in the Cu host and performed a relativistic treatment of impurity scattering based on the solution of the Dirac equation for the muffin-tin model. Nevertheless, approximate muffin-tin potentials were constructed for substitutional impurities in Cu by superposition of atomic potentials. Thus, the lack of a self-consistent solution for the impurity problem, including charge relaxation around the impurity, seems to be the main reason for this discrepancy. In addition, we present our results for the momentum relaxation time τ (Table I) to make a comparison with T_1. In the case of Au impurities, both relaxation times are already of the same order of magnitude. The reason is that the momentum scattering is quite weak since Au and Cu are isovalent. At the same time, the spin-flip scattering is much stronger for Au with respect to other impurities because of the large atomic number of Au.

Monod and Schultz[20] made estimations based on the virtual bound state (VBS) model, including the spin-orbit interaction. The obtained values for the spin-flip scattering cross section are reasonable but do not quantitatively reproduce

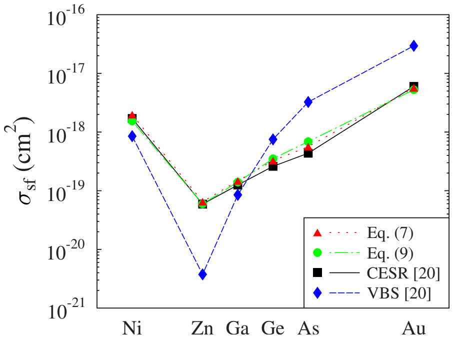

FIG. 1. (Color online) Spin-flip scattering cross section for impurities in bulk Cu (the ordinate is a logarithmic scale). The lines are to guide the eyes.

the experimental situation.[20] We performed calculations of σ_{sf} by using Eq. (7), with the values of $\tau^{\mathrm{sf}}=2T_1$ taken from Table I, and by using Eq. (9) for comparison. Figure 1 shows σ_{sf} for bulk Cu with different types of impurities obtained by our calculations. For comparison, the values derived from the experimental data[20] and the estimations based on the VBS model[20] are shown. We emphasize that the spin-flip scattering cross section used in Ref. 20 is actually twice the σ_{sf}. To follow the calculation of Ref. 20, we use for Eq. (7) the same value of the averaged Fermi velocity $v_F=1.57\times 10^8$ cm/s taken from Ref. 31, while $v_F=1.1\times 10^8$ cm/s was obtained in our calculation. The corresponding scaling procedure was also applied to Eq. (9) to ensure a correct comparison of σ_{sf} values.

It is obvious from Fig. 1 that Eq. (9) provides a good agreement with the results obtained by applying Eq. (7) as well as with the experimental data. Moreover, as shown in Table II, the experiment can be well reproduced by restricting the sum of Eq. (9) to the $l=2$ (*d* electrons) term only for Ni impurities and to the $l=1$ (*p* electrons) term only for the *sp* impurities considered. For Au impurities, the $l=1$ and the $l=2$ terms are of comparable orders due to the large atomic number. Thus, the assumption made in Ref. 20, taking into account merely one type of scattered electron (*p* or *d*), is quite reasonable. The main reason for the deviation of the VBS model from experiment is the lack of charge relaxation around the impurity. The atomic parameters for the spin-orbit constant and the phase shifts for an impurity atom differ remarkably from those for an isolated atom. In particular, the spin-orbit constant for *p* electrons at Zn impurities used in Ref. 20 was assumed to be 48 meV, whereas our self-consistent calculation gives 180 meV.

TABLE II. The *l*-decomposed spin-flip scattering cross section $\sigma_{\mathrm{sf}}(l)$ for impurities in Cu according to Eq. (9). All values are given in cm^2.

Impurity	$\sigma_{\mathrm{sf}}(l=1)$	$\sigma_{\mathrm{sf}}(l=2)$	$\sigma_{\mathrm{sf}}(l=3)$
Ni	3.2×10^{-20}	2.2×10^{-18}	3.1×10^{-29}
Zn	8.1×10^{-20}	4.6×10^{-21}	4.4×10^{-29}
Ga	2.0×10^{-19}	8.1×10^{-22}	7.0×10^{-29}
Ge	5.0×10^{-19}	3.8×10^{-22}	1.1×10^{-28}
As	9.8×10^{-19}	2.8×10^{-22}	1.5×10^{-28}
Au	5.3×10^{-18}	2.2×10^{-18}	2.8×10^{-25}

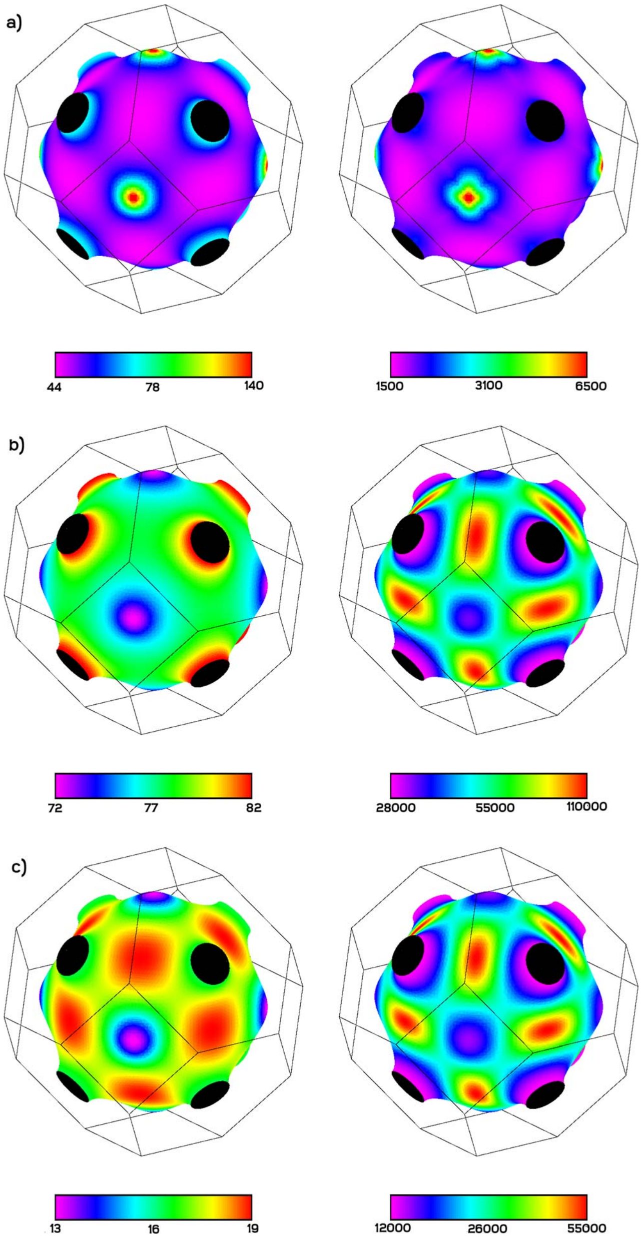

FIG. 2. (Color online) Anisotropic τ (left) and T_1 (right) on the Fermi surface of Cu for (a) Ni, (b) Zn, and (c) Ga impurities with a defect concentration of 1 at. %. All values on the logarithmic scale are given in femtoseconds.

The distributions of the momentum relaxation time τ and the spin relaxation time T_1 on the Fermi surface of Cu are represented in Fig. 2 for Ni, Zn, and Ga impurities. The color scale indicates the increase in relaxation times going from magenta to red. With respect to the Fermi surface of Cu, it is known that the lack of *s* electrons is largest at the necks, the lack of *p* electrons is between the necks, and the lack of *d* electrons is mostly located around the van Hove singularities in the (100) direction.[29] First, let us consider the distribution of τ. The electronic configuration of the impurity atom determines the scattering properties. For example, a Ni impurity is a typical *d* scatterer.[29] It is important to keep in mind that the maximal values correspond to the red areas and indicate weak scattering, while the magenta areas indicate strong scattering. In the case of Ni impurity, the weakest scattering occurs exactly where a d character is missing. Zn and Ga impurities are typical sp scatterers.[29] However, the scattering of s electrons dominates for Zn, and the scattering of p electrons is dominant for Ga. In the case of the spin-flip scattering, according to Eq. (5), s-like electrons do not give any contributions since the spin-orbit interaction vanishes. It is obvious from the top row of Fig. 2 that the momentum and the spin relaxation time show practically the same distribution of scattering strength for Ni impurities. For Zn impurities, the difference is much more pronounced because s electrons dominating the momentum relaxation time do not contribute to the spin relaxation. Spin-flip scattering is weak where a p character is missing, while scattering is strong for the states with a dominant p character. The distributions of the two relaxation times for Ga are quite similar to each other. The picture is determined by p electrons. The corresponding pictures for Ge, As, and Au impurities are qualitatively the same as those for Ga impurities. Actually, as can be seen in Table II, Au impurities cause significant spin-flip scattering contributions in both p and d channels. In general, p electrons dominate for the considered sp scatterers.

In summary, we have performed *ab initio* calculations of the spin relaxation time and the corresponding scattering cross section of the conduction electrons in bulk Cu containing different types of impurities within the Born approximation for the spin-flip transition matrix. The obtained results are in good agreement with CESR experiments.[20] Generally, the spin relaxation time is smaller by several orders of magnitude in comparison to the momentum relaxation time, except for heavy impurities such as Au where spin and momentum relaxation times are of the same order of magnitude. As in the case of the momentum relaxation time, there is a strong relation between the distribution of the spin relaxation time over the Fermi surface and the electronic properties of the impurity atom. The spin-flip scattering is dominated by d electrons for Ni impurities, by p electrons for Zn, Ga, Ge, and As impurities, and by electrons of both characters for Au impurities. It is shown that the self-consistent solution of the impurity problem, including charge relaxation, is essential in properly describing the spin relaxation time.

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[1] *Semiconductor Spintronics and Quantum Computation*, edited by D. D. Awschalom, D. Loss, and N. Samarth (Springer-Verlag, Berlin, 2002).

[2] G. A. Prinz, Science **282**, 1660 (1998).

[3] S. A. Wolf, D. D. Awschalom, R. A. Buhrmann, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488 (2001).

[4] F. J. Jedema, H. B. Heersche, A. T. Filip, J. J. A. Baselmans, and B. J. van Wees, Nature (London) **416**, 713 (2002).

[5] T. Kimura, J. Hamrle, and Y. Otani, Phys. Rev. B **72**, 014461 (2005).

[6] T. Kimura, Y. Otani, T. Sato, S. Takahashi, and S. Maekawa, Phys. Rev. Lett. **98**, 156601 (2007).

[7] L. Vila, T. Kimura, and Y. C. Otani, Phys. Rev. Lett. **99**, 226604 (2007).

[8] T. Valet and A. Fert, Phys. Rev. B **48**, 7099 (1993).

[9] A. Fert and S. F. Lee, Phys. Rev. B **53**, 6554 (1996).

[10] Y. K. Kato, R. C. Myers, A. C. Gossard, and D. D. Awschalom, Science **306**, 1910 (2004).

[11] J. Fabian and S. Das Sarma, J. Vac. Sci. Technol. B **17**, 1708 (1999).

[12] R. J. Elliott, Phys. Rev. **96**, 266 (1954).

[13] Y. Yafet, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 14.

[14] M. I. D'yakonov and V. I. Perel', JETP Lett. **13**, 467 (1971); Phys. Lett. **35A**, 459 (1971).

[15] J. E. Hirsch, Phys. Rev. Lett. **83**, 1834 (1999).

[16] S. Zhang, Phys. Rev. Lett. **85**, 393 (2000).

[17] F. Bloch, Phys. Rev. **70**, 460 (1946).

[18] F. J. Dyson, Phys. Rev. **98**, 349 (1955).

[19] T. W. Griswold, A. F. Kip, and C. Kittel, Phys. Rev. **88**, 951 (1952).

[20] P. Monod and S. Schultz, J. Phys. (Paris) **43**, 393 (1982).

[21] J. R. Asik, M. A. Ball, and C. P. Slichter, Phys. Rev. Lett. **16**, 740 (1966).

[22] N. A. W. Holzwarth and M. J. G. Lee, Phys. Rev. B **13**, 2331 (1976).

[23] Y. Yafet, J. Appl. Phys. **39**, 853 (1968).

[24] N. Papanikolaou, N. Stefanou, P. H. Dederichs, S. Geier, and G. Bergmann, Phys. Rev. Lett. **69**, 2110 (1992).

[25] P. Zahn, J. Binder, I. Mertig, R. Zeller, and P. H. Dederichs, Phys. Rev. Lett. **80**, 4309 (1998).

[26] L. Szunyogh, B. Újfalussy, P. Weinberger, and J. Kollár, Phys. Rev. B **49**, 2721 (1994).

[27] N. Papanikolaou, R. Zeller, and P. H. Dederichs, J. Phys.: Condens. Matter **14**, 2799 (2002).

[28] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[29] I. Mertig, Rep. Prog. Phys. **62**, 237 (1999).

[30] The factor of 2/3 is missing in expression (2) of Ref. 24, which corresponds to our Eq. (8). It seems to be the reason why, as written in Ref. 24, "the experimental values lie about 30% below the theoretical ones" in the case of the Mg host. So, the approach used in Ref. 24 should give a better agreement with the experiment than what was presented there. Our expression is based on Ref. 23.

[31] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt-Saunders, New York, 1976).