First-Principles Calculations of the Spin-Orbit Scattering Cross Section of *sp* Impurities in Mg

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The spin-orbit scattering of 4*sp* and 5*sp* impurities in a Mg host is investigated theoretically by self-consistent local-density-functional theory. The calculated spin-orbit scattering cross sections σ_{SO} agree with the available experimental results for low valent impurities. For higher valent impurities we predict a *p* resonance behavior. For Cu and Ag impurities our results point to errors of density-functional theory in estimating the *d* contribution to σ_{SO}. In total a consistent interpretation of the trends is given.

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Spin-orbit interaction plays an important role in solid-state physics. It leads to a coupling between the directions in real space and in spin space, and its strength determines whether the electron spin is a good quantum number. From the Knight shift in disordered superconductors to the calculation of the upper critical field B_{c_2}, the destruction of the Clogston limit, and formation of spin-polarized excitations in high magnetic fields, the whole field of superconductivity is strongly influenced by the spin-orbit scattering (SOS). But there are other areas in solid-state physics such as the Hall effect of liquid metals and the anomalous Hall effect which are, according to our present understanding, determined by the SOS processes. Spin-orbit interaction also plays an important role in magnetism, since it strongly influences the magnetic anisotropy and, e.g., determines the magneto-optical properties. Despite its importance for many phenomena in solids the theoretical treatment of SOS has been widely neglected. The present paper represents a contribution to this field.

Recently two of us measured the SOS cross section σ_{SO} of many *sp* impurities in disordered Mg films [1]. In this experiment the method of weak localization has been used to determine the spin-flip scattering due to the impurities. The beauty of the method is that it allows a direct determination of the scattering by the spin-orbit potential of the impurities, since the dominating potential scattering does not destroy the coherence of the backscattered wave. Motivated by these results we calculate in this paper the SOS cross sections for 4*sp* and 5*sp* impurities in Mg. With the exception of the old work of Abrikosov and Gorkov [2], predicting a proportionality to the fourth power of the atomic number, no theoretical treatment of the SOS due to impurities exists. In our calculation we treat the Mg host as a jellium. This appears to be well justified since in the experimental investigation quench-condensed Mg films were used as the host material for the impurities. Such films have a very short mean free path and therefore they should be a good example for the jellium model because the anisotropy of the nearly-free-electron band structure of the Mg host [3] is essentially washed out by the short mean free path.

The main results of our calculations are the following: (i) We get good agreement with the experimental results for low valent impurities. (ii) For higher valent impurities we predict a resonance maximum of the SOS, in contradiction to the previously assumed monotonic behavior [1,2]. (iii) We give a consistent interpretation of the calculated trends and point out an error of local-density-functional theory in overestimating the *d* contributions for the noble metal impurities.

In the case of 4*sp* and 5*sp* elements the spin-orbit interaction

$$V_{\mathrm{SO}}(r)=\frac{1}{c^2 r}\frac{dV(r)}{dr}\mathbf{L}\cdot\mathbf{S} \tag{1}$$

can be treated as a perturbation to the nonrelativistic Hamiltonian. In this paper Rydberg atomic units are used, i.e., the velocity of light c equals 274.074. A consequence of including spin-orbit interaction is that the spin $\mathbf{S}$ and angular momentum $\mathbf{L}$ are no longer conserved. Instead, the magnetic quantum number of the total angular momentum $\mathbf{J}=\mathbf{L}+\mathbf{S}$ is conserved. Therefore the potential introduces phase shifts $\delta_{j,l}^{\mathrm{SO}}$ for the asymptotic wave function which depend on both the total $(j=l\pm\frac{1}{2})$ and orbital (l) angular momentum quantum numbers. The SOS cross section can be expressed in terms of these phase shifts [4],

$$\sigma_{\mathrm{SO}}=\frac{4\pi}{E_F}\sum_l\frac{l(l+1)}{2l+1}\sin^2\{\delta_{l+1/2,l}^{\mathrm{SO}}(E_F)-\delta_{l-1/2,l}^{\mathrm{SO}}(E_F)\}\ , \tag{2}$$

where E_F is the Fermi level of the host ($E_F=k_F^2$ in Rydberg units).

The one-electron spherically symmetric potential of the impurity, $V(r)$, is calculated self-consistently by solving iteratively the nonrelativistic Kohn-Sham equations [5]. Exchange and correlation effects are included within the local-density approximation of Hedin and Lundqvist [6]. Using a range $S=10$ a.u. of the impurity potential and an angular momentum cutoff $l_{\max}=3$, we obtain good convergence in all cases examined. The Friedel screening rule is satisfied within a few percent. Details about our calculational method can be found elsewhere [7].

The scattering t matrix

$$t_{j,l}^{\mathrm{SO}}(E) = -\frac{1}{\sqrt{E}} \exp\{i\delta_{j,l}^{\mathrm{SO}}(E)\} \sin\{\delta_{j,l}^{\mathrm{SO}}(E)\} \tag{3}$$

is given to first order in the spin-orbit interaction by the equation

$$t_{j,l}^{\mathrm{SO}}(E) \cong t_l(E) + \int_0^S R_l^2(r;E) \left\{ \begin{matrix} l \\ -l-1 \end{matrix} \right\} \frac{1}{c^2 r} \frac{dV(r)}{dr} r^2 dr \,, \tag{4}$$

where the factors l and $-l-1$ are used for $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$, respectively. $R_l(r;E)$ are self-consistently calculated complex radial wave functions of the unperturbed (without spin-orbit interaction) system with the appropriate asymptotic behavior [7] and $t_l(E)$ are the corresponding scattering t matrices for potential scattering.

The SOS cross section of 4sp and 5sp impurities is calculated using Eqs. (2), (3), and (4). The first-order Born approximation can be justified from our results, since the integral in Eq. (4) is in most cases one order of magnitude smaller than t_l. Our results for σ_{SO} are shown in Fig. 1 together with the experimental data. Within a given sp series of impurities the SOS cross section shows a parabolic behavior with a maximum in the middle of the series. The parabolic curve is shifted to higher values of σ_{SO} when we consider impurities from the next row of the periodic table.

A comparison between the experimentally measured and the theoretically calculated cross section yields on an average that, with the exception of Cu and Ag impurities, the experimental values lie about 30% below the theoretical ones. We consider this a remarkable agreement because in the experiment the method of weak localization was used to determine the SOS time with absolute accuracy. For more details we refer to [1]. There are very few examples in which the absolute time scale of weak localization has been checked and we consider the agreement between the experimental and theoretical results very encouraging.

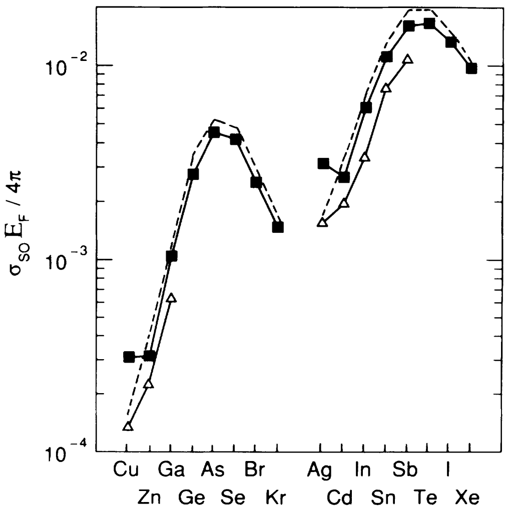

FIG. 1. Spin-orbit scattering cross section of 4sp and 5sp impurities in Mg. The squares show our theoretical results and the triangles the experimental data (Ref. [1]). The dashed line shows the p contribution alone as calculated in the approximation (9).

From the agreement between experiment and theory we conclude that the theory describes the underlying physics very well. Next, in order to understand the behavior of the SOS cross section, we proceed with some approximations of the above formulas.

In the cases examined, the sinus of the difference of the phase shifts in Eq. (2) can be adequately approximated by the argument. Moreover, one can show that to first order in the spin-orbit interaction one obtains for $l \geq 1$

$$\delta_{l+1/2,l}^{\mathrm{SO}}(E_F) - \delta_{l-1/2,l}^{\mathrm{SO}}(E_F) \simeq (2l+1) E_F^{1/2} \xi_l(E_F) \,, \tag{5}$$

where

$$\xi_l(E_F) = \int_0^S |R_l(r;E_F)|^2 \frac{1}{c^2 r} \frac{dV(r)}{dr} r^2 dr \,. \tag{6}$$

In the case of sp impurities, where the p-electron SOS is most important, significant contributions to the integral in Eq. (6) arise only from the region near the origin. Indeed, by restricting the integration up to the distance of the first node of the p wave function from the origin (0.1-0.2 a.u.), the error in the calculation of the p contribution to σ_{SO} is less than 2%. In the region near the origin, the self-consistent potential is essentially determined by the Coulomb attraction from the nucleus $V_c(r) = -2Z/r$. Therefore, by introducing the impurity local density of states within the atomic sphere $(0, R_{\mathrm{WS}})$

$$n_l(E) = \frac{2\sqrt{E}}{\pi} (2l+1) \int_0^{R_{\mathrm{ws}}} |R_l(r;E)|^2 r^2 dr \tag{7}$$

and the matrix element of r^{-3},

$$M_l(E) = \frac{\int_0^{R_{\mathrm{ws}}} |R_l(r;E)|^2 r^{-3} r^2 dr}{\int_0^{R_{\mathrm{ws}}} |R_l(r;E)|^2 r^2 dr} \,, \tag{8}$$

we finally obtain for the SOS cross section

$$\sigma_{\mathrm{SO}} \simeq \frac{\pi^3}{E_F} \left(\frac{2Z}{c^2} \right)^2 \sum_l \frac{l(l+1)}{2l+1} \{M_l(E_f)\}^2 \{n_l(E_F)\}^2 \,. \tag{9}$$

Note that the matrix element depends only on the radial form of the wave function, but not on its amplitude. In contrast to this, $n_l(E_F)$ depends only on the amplitude, determining the occupancy of the orbital. Because of the additional approximations, this expression for the SOS cross section is not very accurate and only serves pedagogical purposes.

The partial densities of states $n_l(E_F)$ and the matrix elements $M_l(E_F)$ are collected in Table I. The contribu-

TABLE I. Partial densities of states $n_l(E_F)$ (states/Ry atom) and matrix elements $M_l(E_F)$ (in a.u.$^{-3}$) for 4*sp* and 5*sp* impurities in Mg. [Note that $M_s(E_F)\equiv 0$.]

Impurity	$n_s(E_F)$	$n_p(E_F)$	$n_d(E_F)$	$n_f(E_F)$	$M_p(E_F)$	$M_d(E_F)$	$M_f(E_F)$
Cu	1.67	3.22	1.71	0.12	3.93	8.00	0.06
Zn	1.25	4.30	0.83	0.13	4.56	3.46	0.05
Ga	0.77	5.85	0.93	0.14	5.78	1.38	0.05
Ge	0.49	6.86	1.06	0.14	7.70	0.83	0.05
As	0.37	6.14	1.16	0.14	10.54	0.60	0.05
Se	0.33	3.98	1.29	0.14	14.90	0.51	0.05
Br	0.36	2.05	1.57	0.15	21.61	0.50	0.04
Kr	0.46	1.17	2.19	0.17	28.05	0.56	0.04
Ag	1.47	2.84	1.15	0.14	9.15	9.54	0.05
Cd	1.24	3.70	0.82	0.15	9.83	6.40	0.04
In	0.91	4.67	0.93	0.17	11.15	3.71	0.06
Sn	0.65	5.16	1.15	0.19	13.17	2.63	0.05
Sb	0.46	4.83	1.41	0.20	16.25	1.95	0.07
Te	0.36	3.69	1.77	0.21	20.82	1.65	0.08
I	0.32	2.39	2.33	0.24	27.68	1.54	0.08
Xe	0.32	1.48	3.34	0.27	36.97	1.59	0.12

tion of the *s* states to the SOS vanishes identically. The general behavior is dominated by the contribution of the *p* states as can be seen from the dashed curve in Fig. 1, which shows the *p* contribution alone as calculated in the approximation (9). Exceptions are the cases of Cu and Ag where the *d* states also give a significant contribution. Within a given row of impurities, e.g., the 4*sp* row, the trend of $\sigma_{\rm SO}$ is essentially determined by the behavior of the *p* local density of states (LDOS) of the impurity at E_F, despite the fact that Z and $M_p(E_F)$ increase monotonously. This density of states is characterized by a *p* resonance peak which results from the hybridization of the atomic *p* states of the impurity with the host free electron gas. For the early 4*sp* impurities this resonance is situated above E_F and it is very broad due to the strong hybridization with the host. As we move along the 4*sp* row of impurities the *p* states are progressively occupied. The *p* peak shifts inwards and becomes sharper, since the hybridization with the host is reduced due to the increasing localization of the impurity *p* state and the decrease of the host density of states. Thus, in the case of Br impurity, for instance, $n_p(E)$ exhibits a sharp peak near the bottom of the band and for Kr we have a bound *p* state. The *s* and *d* LDOS evolve similarly, as shown in Fig. 2. The observed maximum of $\sigma_{\rm SO}$ in the middle of an *sp* row indicates the crossing of the *p* resonance through the Fermi energy. However, as can be seen from Table I, the maximum of $n_p(E_F)$ arises for Ge(Sn) whereas the $\sigma_{\rm SO}$ curve has its maximum for As(Sb), respectively. This shift of the maximum is due to the variation of $\{ZM_p(E_F)\}^2$ within a given series. The strong increase of $M_p(E_F)$ in each row arises from the increasing contraction of the *p* wave function. In contrast to this, the *d* matrix element strongly decreases at the beginning of the series which is connected to the change of the character of the wave function at E_F from 3*d* to 4*d*, 4*d* to 5*d*, respectively. By comparing two different rows, e.g., 4*sp* versus 5*sp*, $n_p(E_F)$ is more or less the same, but Z and $M_p(E_F)$ increase. The increase of $M_p(E_F)$ can be understood since for the 5*sp* impurities the first node of the *p* wave func-

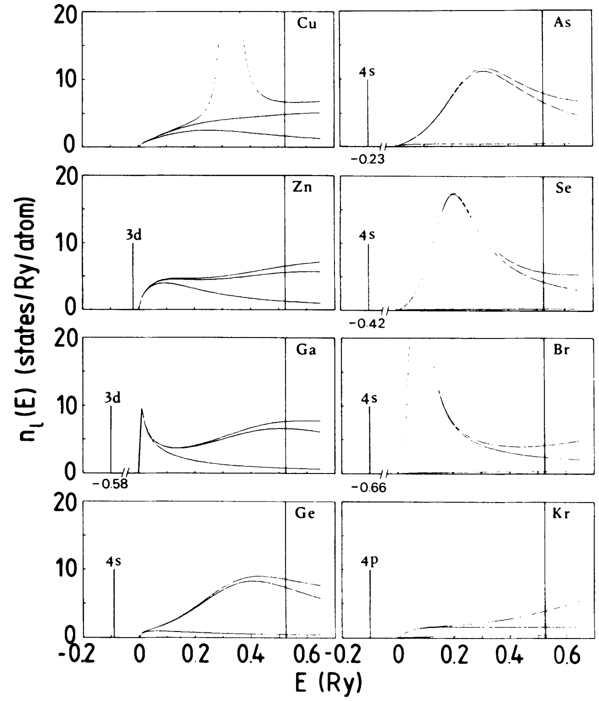

FIG. 2. Local densities of states (*s*, *s*+*p*, and total LDOS from bottom to top) of 4*sp* impurities in Mg. The bound states are shown as vertical bars and the attached number gives their position. The vertical lines on the abscissa indicate the Fermi energy (E_F=0.524 Ry).

tion is closer to the origin than the one of the 4*sp* impurities.

The disagreement found in the calculations for Cu and Ag impurities (see Fig. 1) is caused by an error of the local density approximation, which always yields too high values for localized *d* states. For instance, the calculated *d* band of pure Cu lies about 0.5 eV higher than experimentally observed, whereas for Cu impurities in Al [8] the error is more than 1 eV. However, if the virtual bound state is shifted to lower energies, both the density of states $n_d(E_F)$ and the matrix element $M_d(E_F)$ would decrease, so that the agreement with experiment would improve.

In summary, our results yield a consistent interpretation of the available experimental data and enable physical insight into the SOS process. In particular, we predict a *p* resonance for impurities from the middle of the *sp* series and point out that local-density calculations overestimate the *d* contribution for noble-metal impurities. Experimental investigations for higher valent impurities are highly desirable to confirm the resonance behavior.

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