Residual Atomic Behavior of (*sp*) Impurities in a Mg Host

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The spin-orbit scattering cross section of many different impurities (Cu, Zn, Ga, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi) in Mg is measured by means of weak localization. We find two distinct dependences of $\sigma_{s.o.}$. (i) For the same valence of the impurity $\sigma_{s.o.}$ shows a power law as a function of the atomic number Z as Z^p with $p \simeq 5$ for the noble metals, and (ii) $\sigma_{s.o.}$ depends on the valence of the impurity; for s impurities $\sigma_{s.o.}$ is considerably smaller than for p impurities. This suggests that the atomic electronic wave functions are quite well preserved after dissolving the atom.

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Impurities are the most common defects in "pure" materials and, in many cases, they alter the properties of the host considerably. In particular impurities determine the transport properties of a material. Therefore impurities have been studied with many different methods, such as transport measurements, nuclear resonance, extended x-ray-absorption fine structure, electron-spin resonance, de Haas–van Alphen effect, and many more.

One of the fascinating problems for an impurity dissolved in a host is the question: How many of its atomic properties are conserved and which of its atomic properties have disappeared? This question has been intensively studied for magnetic d and f impurities. In the atom the electronic states are described not only by the quantum numbers of the individual electrons (such as l and s) but also by the quantum numbers of the total angular momentum L and total spin S. Their occupation is governed by Hund's rules. If one dissolves the atom in a host metal then the individual (atomic) electron states hybridize with the conduction electrons. This behavior is described by Friedel's phase shifts δ_l which depend on the orbital angular momentum of the electronic state. For impurities with a partially filled d shell one obtains a d resonance which splits for magnetic d impurities into two subbands for spin up and spin down. Although Hund's rules appear to be less stringent for such d impurities, one can surely recognize the original d character of the atom. On the other hand, $4f$ impurities appear to conserve their atomic character much better. For s and p impurities the question of conserving atomic properties has not been studied because there appeared to be very few methods for its investigation. We will assume that the electronic wave functions of an atom have the configuration $s^v p^{v'}$. Now we dissolve this atom as an impurity in a host. Then the question arises whether the electronic wave functions of the impurity are still $s^v p^{v'}$ like. As we will see below we can study this question by means of the spin-orbit scattering cross section of the impurity atom.

There is very little known about the spin-orbit scattering in metals. Abrikosov and Gorkov [1] suggested several decades ago that the spin-orbit scattering strength in metals with disorder is proportional to the fourth power of the atomic number. So far the only systematic investigation has been performed for pure metals with lattice defects by Meservey and Tedrow [2] using polarized electrons in superconducting tunneling junctions. The Z^4 law as suggested by Abrikosov and Gorkov was only intended as a rule of thumb. It would be very surprising if there is no dependence of the spin-orbit scattering cross section on the valence of the impurity. Obviously the spin-orbit scattering of impurities deserves more experimental and theoretical attention.

In this paper we study the spin-orbit scattering cross section of many (s,p) impurities (Cu, Zn, Ga, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi) in Mg. We determine the spin-orbit scattering cross section with the method of weak localization (see, for example, the review articles [3–6]). Magnetoresistance measurements of disordered thin films, corresponding to a time-of-flight experiment with conduction electrons [7], permit the measurement of the spin-orbit scattering time.

In the experiment we first condense a thin film of about 30 atomic layers of Mg onto a quartz plate which is at helium temperature. Then we evaporate on top of the Mg film a fraction of a monolayer of the impurity. The thickness of the impurity lies between 0.1 and 0.05 atomic layer. Only for Cu and Zn, which have a very small spin-orbit scattering cross section, do we need about 1 and 0.5 atomic layer of the impurity, respectively. For obtaining the desired coverage of the impurity the impurity material was heated in a tantalum or tungsten boat and its evaporation rate was determined over a period of several minutes. An evaporation rate between 0.1 and 1 monolayer/min was chosen. Then the shutter was electronically opened for a period between 10 s and 1 min so that the desired coverage was achieved. The accuracy of the impurity coverage is estimated to be about 20%.

In the last step the impurities are covered with five atomic layers of Mg so that they behave as bulk impurities. (In this paper we do not discuss the spin-orbit scattering of surface impurities.) All these evaporations are performed *in situ* at low temperature in ultrahigh vacuum, better than 10^{-11} Torr. After each evaporation step the sandwich was annealed (the first film up to 40 K and the sandwiches to 35 K). Afterwards the magnetoresistance is measured for several temperatures between

4.5 and 20 K. Figure 1 shows the magnetoresistance curves for pure Mg and Mg films with Ag and Au impurities (measured at 4.5 K). The impurity concentration is about 1.5×10^{-3} (corresponding to a coverage of 0.05 atomic layer of the impurity). The corresponding magnetoresistance curve for Mg with the same concentration of Cu is almost identical with the one for pure Mg. One recognizes the formation of the spin-orbit scattering minimum with increasing atomic number Z. (Similar magnetoresistance curves have been shown in previous papers [5] and the agreement between experiment and theory is, as usual for quench condensed films, very good.)

The evaluation of the magnetoresistance yields a magnetic field $H_{s.o.}$ which represents the strength of the spin-orbit scattering and permits the calculation of the spin-orbit scattering time $\tau_{s.o.}$ by means of the relation $H_{s.o.}\tau_{s.o.}=\hbar epN/4$, where ρ is the resistivity of the film and N is the density of states at the Fermi level (for both spins). This spin-orbit scattering field for pure Mg is only 0.005 T because Mg has a small atomic number Z. We chose the coverage of the impurities sufficiently large so that their additional contribution $\Delta H_{s.o.}$ to the spin-orbit scattering was at least as large as that of pure Mg. This minimizes the error in the determination of $\Delta H_{s.o.}$.

The impurity coverage yields the concentration of the impurities n_i and $\Delta H_{s.o.}$ yields the spin-orbit scattering time $\tau_{s.o.}$ and the corresponding mean free path $l_{s.o.}$. Using the relation $\sigma_{s.o.}l_{s.o.}n_i=1$ one obtains for the spin-orbit scattering cross section (within the free-electron model) the relation

$$\sigma_{s.o.}=\frac{\Omega^{2/3}}{d_i}\frac{\Delta H_{s.o.}}{R}\frac{1}{\epsilon_F}\frac{2\pi^2\hbar^2}{em}, \tag{1}$$

where Ω is the atomic volume of the impurity, d_i the coverage of the impurity in units of atomic layers, ϵ_F the Fermi energy, R the resistance per square of the film, and $\Delta H_{s.o.}$ the spin-orbit scattering field induced by the impurities.

For most impurities the experimental concentration is sufficiently small to obtain $\sigma_{s.o.}$ of the single impurity. Even for Cu and Zn where we were required to use a considerably higher concentration the spin-orbit scattering cross section was within the experimental accuracy independent of the Cu and Zn coverage.

In Fig. 2 we have plotted the spin-orbit scattering cross section $\sigma_{s.o.}$ as a function of the atomic number Z on a double logarithmic scale. One recognizes that each impurity row (the $4sp$, the $5sp$, and the $6sp$ row) shows a strong increase of the spin-orbit scattering cross section with increasing valence. If we compare impurities with the same valence as a function of Z, we find a strong increase with increasing Z. For the noble metals we find a power law of roughly $\sigma_{s.o.}\simeq Z^5$.

Since our quench condensed Mg films have a very short mean free path, they should be a good example for a jelli-

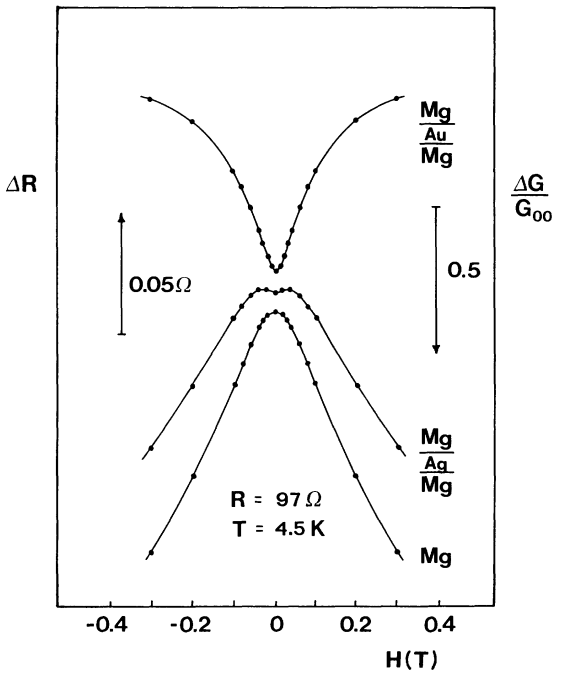

FIG. 1. Magnetoresistance curves [i.e., the conductance $G(H)/G_{00}$ ($G_{00}=e^2/2\pi^2\hbar$) using the right scale] for pure Mg and Mg films with Ag and Au impurities (impurity concentration about 1.5×10^{-3}). The points represent the experimental results and the solid curves are theoretical fits.

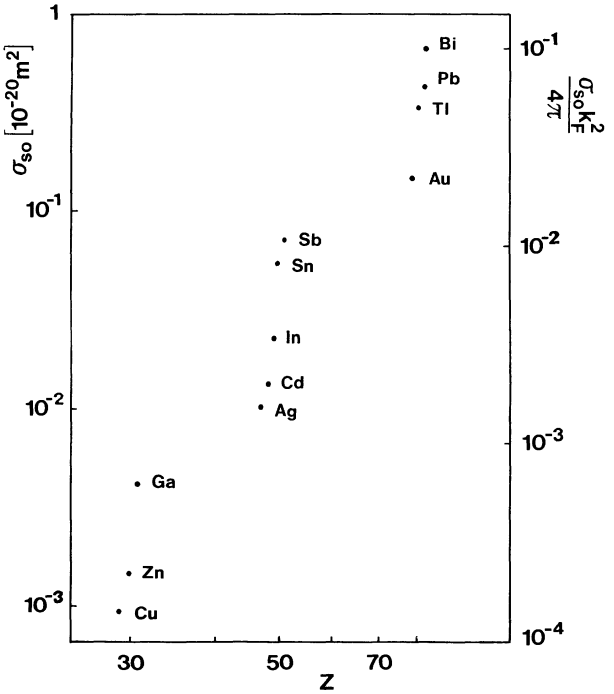

FIG. 2. The spin-orbit scattering cross section of different (s,p) impurities in Mg on a log-log plot. The right scale is discussed in the text.

um model because the anisotropy of the band structure is essentially washed out by the short mean free path. Therefore we may treat the impurity as being dissolved in a jellium. As a consequence, we can assume that the potential of the impurity is spherically symmetric. For heavy impurities the electrons feel besides the potential also a spin-orbit interaction. This means that the magnetic quantum number of the orbital angular momentum and the spin are no longer conserved. Instead, the magnetic quantum number of the total angular momentum is conserved. Therefore the potential introduces phase shifts $\delta_{j,l}$ for the asymptotic wave function which depends on both the total angular momentum $j=l\pm\frac{1}{2}$ and the orbital angular quantum number l. These phase shifts can be numerically calculated from the potential of the impurities and the density of the jellium.

For the interpretation of our experimental data we derived the spin-orbit scattering cross section as a function of the phase shifts $\delta_{l\pm 1/2,l}$. The final result for $\sigma_{s.o.}$ is

$$\sigma_{s.o.}=\frac{4\pi}{k_F^2}\sum_l \frac{l(l+1)}{2l+1}\sin^2(\delta_{l+1/2,l}-\delta_{l-1/2,l})\,. \qquad (2)$$

The spin-orbit scattering cross section is proportional to $\sin^2(\delta_{l+1/2}-\delta_{l-1/2})$. In most practical cases this can be approximated by $(\delta_{l+1/2}-\delta_{l-1/2})^2$. In Fig. 2 the right ordinate corresponds to a plot of $\sigma_{s.o.}k_F^2/4\pi$ which represents the experimental result for the sum over l in Eq. (2).

In Fig. 3 we have plotted a renormalized spin-orbit scattering cross section $\sigma^*_{s.o.}$ as a function of the valence for the $5sp$ impurities. The original $\sigma_{s.o.}$ is divided by

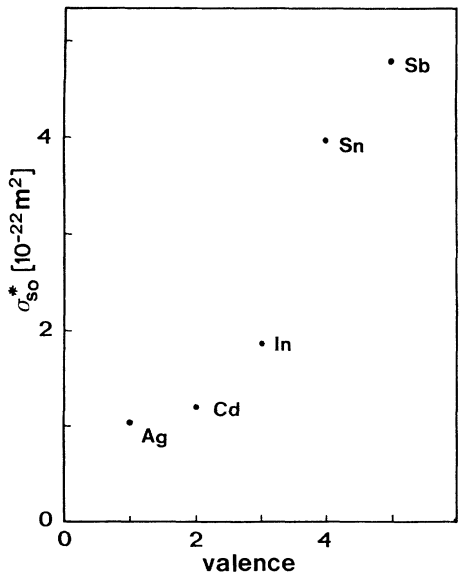

FIG. 3. The spin-orbit scattering cross section of $5sp$ impurities as a function of the valence. The dependence on the atomic number Z has been compensated for (see text).

$(Z/47)^5$ to compensate for the effect of increasing nuclear charge and to extract only the influence of the valence on $\sigma_{s.o.}$. We consider first the impurities Ag and Cd with the valences one and two. In the atom the valence electrons have the states s^1 and s^2, i.e., they possess the angular momentum zero. As we recognize from Fig. 3, the spin-orbit scattering cross section for the s impurities is considerably smaller than the cross section for the p impurities In, Sn, and Sb. The p electrons with the angular momentum $l=1$ contribute considerably more strongly to $\sigma_{s.o.}$. We conclude that the impurities Ag and Cd essentially maintain their s states in the host. On the other hand, their $\sigma_{s.o.}$ is not zero. Therefore we recognize that a fraction of the electron states occupy the p states and possibly even the d states. Furthermore, we conclude that for the p impurities In, Sn, and Sb the p states are progressively occupied.

As we pointed out above, the contribution to $\sigma_{s.o.}$ vanishes for s-like impurity states. This explains very elegantly why $\sigma_{s.o.}$ is considerably smaller for the one and two valence impurities. However, for a quantitative evaluation of Eq. (2) and a comparison with the experimental results a relativistic calculation has to be performed using the atomic potential of the impurity and adjusting the chemical potential of the host with respect to the atomic potential. There exist sophisticated methods to calculate the electronic properties of impurities in a host metal [8,9]. They are mostly used to calculate the magnetic properties of the impurity but should also work for the calculation of the spin-orbit scattering. We hope that our measurements stimulate such calculations. As a matter of fact, we believe that the theoretical treatment of the spin-orbit scattering has been strongly neglected in the theory of solid-state physics. The strength of the spin-orbit scattering plays an important role in many areas of solid-state physics because it 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_{c2}, 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 spin-orbit scattering. But there are other areas in solid-state physics such as the Hall effect of heavy liquid metals like Tl, Pb, and Bi which show a deviation from the free-electron Hall constant (for a survey see, for example, [10,11]). Furthermore, the Hall effect of liquid transition metals and the anomalous Hall effect are, according to our present understanding, determined by the spin-orbit scattering processes.

We recently started a collaboration with the groups of Dederichs and Stefanou. They have extensive experience in calculating the properties of d impurities in different host metals. These calculations can also be applied to calculate the phase shifts of the total angular momentum. Therefore we hope that shortly a comparison between our

experimental results and a first-principles calculation will be possible. We believe that it will considerably enrich our understanding of the properties of simple impurities in a host metal.

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[1] A. A. Abrikosov and L. P. Gorkov, Zh. Eksp. Teor. Fiz. **42**, 1567 (1962) [Sov. Phys. JETP **15**, 1088 (1962)].
[2] R. Meservey and P. M. Tedrow, Phys. Lett. **58A**, 131 (1976).
[3] B. L. Altshuler, A. G. Aronov, D. E. Khmelnitskii, and A. I. Larkin, in *Quantum Theory of Solids,* edited by I. M. Lifshits (Mir, Moscow, 1982), p. 130.
[4] H. Fukuyama, Surf. Sci. **113**, 489 (1982).
[5] G. Bergmann, Phys. Rep. **107**, 1 (1984).
[6] P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).
[7] G. Bergmann, Phys. Rev. B **28**, 2914 (1983).
[8] S. Bluegel, B. Drittler, R. Zeller, and P. H. Dederichs, Appl. Phys. A **49**, 547 (1989).
[9] N. Stefanou and N. Papanikolaou (to be published).
[10] L. E. Ballentine and M. Huberman, J. Phys. C **10**, 4991 (1977).
[11] M. Huberman and L. E. Ballentine, Can. J. Phys. **56**, 704 (1978).