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Conduction electron spin-flip scattering by impurities in copper (*)

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Abstract. — We have measured the concentration dependence of the transmission conduction electron spin resonance linewidth of copper doped with Li, Zn, Ga, Ge, As, Ni, and Ti. In each case, we find a linear concentration dependence which allows us to determine a spin-flip cross-section \( \sigma_{sf} \) for each impurity. These cross-sections, together with those deduced from linewidth data previously published for other impurities (both magnetic and non), form a useful body of results and allow one to test spin-flip scattering models. We find an overall agreement of our values for \( \sigma_{sf} \) for transition metal impurities with estimates based on the Friedel virtual bound state model, including a spin-orbit interaction. For specific impurities (Zn, Ga, Ge, and As) we find that \( \sigma_{sf} \) is determined by the charge contrast between the impurity and the copper host as was noted earlier from similar studies based on Li and Na by Asik, Ball, and Slichter. A particular situation is present with Li as an impurity in copper, interpreted as a « spin-orbit hole », which, together with the other results, confirm that the spin-orbit difference between the impurity and the host is the relevant spin-orbit parameter for \( \sigma_{sf} \).

1. Introduction. — Soon after the discovery of conduction electron spin resonance (CESR) in metals [1], Elliott [2] proposed that the dominant relaxation mechanism was due to the spin-orbit interaction with impurities. A detailed consideration of this mechanism was presented by Yafet [3]. Feher and Kip [4] provided the first experimental evidence for this impurity effect by showing that the linewidth in Li at room temperature was reduced by successive distillation (via evaporation) and by the temperature dependence of the linewidth in Na.

The first systematic study of the temperature independent electron spin scattering in metals was performed by Asik, et al. [5] who dissolved non-magnetic non-transition metal impurities in Li and Na. From the linear increase in CESR linewidth with impurity concentration they were able to deduce a value for the spin-flip cross-section \( \sigma_{sf} \) in a good agreement with theoretical estimates based on the atomic spin-orbit interaction. A similar type of experimental work and analysis has been reported by Huisjen, et al. [6] who imbedded transition metal impurities in Al. There have been several determinations of spin-flip cross-sections of non-magnetic...
impurities deduced via the linear rate of increase of relaxation of a dilute magnetic alloy in the bottleneck regime as a function of the non-magnetic impurity concentration. These determinations are, in general, in good agreement with the direct method (when both can be used) but offers the advantage of being potentially operative for metals whose spin resonance is unobservable, provided that the magnetic impurities added (Mn, Cr, Gd, Eu) produce a reasonably narrow bottlenecked resonance. This method enables one to readily determine the spin-flip cross-section of the magnetic impurity itself (via a spin non-conserving potential, i.e., excluding exchange). We have assembled in table I a selection of references [6-22] who have measured the spin-flip cross-section of impurities (both non-magnetic and magnetic) present in three important metals not studied by Asik, et al. [5], i.e., Cu, Ag, and Al. A number of extremely scattered results exist in the literature on less studied metal hosts like Au, Mg, or Pd and also a large number of intermetallic compounds. For these results one may refer to the monograph compiled by Taylor [23]; however, it should be noted that the work on dilute magnetic alloys (by transmission) has been systematically dropped from this otherwise very complete set of references.

Our present work, which is similar in principle to that of references [5] and [6], consists of studying the broadening of the copper CESR as a function of adding Li, Zn, Ga, Ge, As, Ti, and Ni. This work was initially motivated by two considerations:

1. The situation studied by both Asik, et al. and Huisjen, et al. corresponds to a low Z host metal (with consequent little intrinsic spin-orbit interaction) into which higher Z impurities are added. An interesting situation occurs if one chooses a medium Z host, such as Cu, which can be doped with impurities of comparable Z (Zn, Ga, Ge, and As), or much lower Z, (Li), or much higher, (Au). An advantage of copper as a host is that its metallurgical properties, in contrast to both the alkalis and Al, allows one to readily dissolve the transition metal impurities as well as those just mentioned.

2. A specific practical motivation for this work stems from the observation that although CESR has been observed in an appreciable number of metals (the alkalis, Be, Mg, Al, Cu, Ag, Au, and Pd), there are many other metals of comparable or even lower impurity content (Cd, In, Sn, W, Pt, Ga, and Nb) for which attempts at observing CESR have been unsuccessful to date [24]. It is thus of interest to have some confidence in the ability to estimate the spin-flip cross-sections for diverse impurity situations (i.e.,

<table>
<thead>
<tr>
<th>Li</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>this work</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>this work</td>
<td>15</td>
<td>7, 18, 13, 14</td>
<td>7, 17 (°), 10</td>
<td>7, 17 (°)</td>
<td>this work</td>
<td>7, 17 (°)</td>
</tr>
<tr>
<td>Ag</td>
<td>22</td>
<td>21</td>
<td>8 (°), 12 (°), 13, 20 (°)</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>(°)</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
<td>Sb</td>
<td>Rare Earth</td>
<td>Gd</td>
<td>Pt</td>
<td>Au</td>
</tr>
<tr>
<td>Cu</td>
<td>this work</td>
<td>this work</td>
<td>this work</td>
<td>19 (°)</td>
<td>19 (°)</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>8</td>
<td>8</td>
<td>(°)</td>
<td>8</td>
<td>12</td>
<td>22</td>
<td>16</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>11</td>
<td>18</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(°) Means that in this reference only the slope of linewidth versus temperature for a dilute magnetic alloy containing the impurity is available. The spin-flip cross-section must be inferred by the reader following a bottleneck analysis. Our own estimate for it is given with the reference, if no better determination is published elsewhere.

(°) The spin-flip cross-section of intrinsic defects (dislocations) has been measured for Cu, Ag, and Al by Beuneu, F. and Monod, P., Phys. Rev. B 13 (1976) 3424, and can be usefully compared to the effect of phonons. A summary: spin-flip scattering by phonons in metals is found in Monod, P. and Beuneu, F., Phys. Rev. B 19 (1979) 911.
charge and spin-orbit contrast) before ascribing this failure to observe CESR to intrinsic factors such as anisotropic $g$-factor over the Fermi surface [25].

A recent motivation stems from the investigation of the effect of non-magnetic impurities on the dynamic properties of spin glasses. Indeed, as is apparent in the systematic work of Okuda and Date [26] impurities with large spin-orbit coupling give rise to both a shift and a width in the observed ESR of CuMn in the spin glass phase. Hence, a special investigation of the elementary spin-orbit scattering by these impurities is highly desirable as emphasized by Fert and Levy [26].

## 2. Experimental procedures

### 2.1 SPECTROMETER

The conduction electron spin properties were measured by the transmission technique (TESR) whereby a very thin sample is made the common wall between a pair of microwave cavities. When the applied dc magnetic field is in the vicinity of resonance, microwave power incident upon the first cavity (transmit) excites some non-equilibrium magnetization which diffuse through the sample and radiates into the second (receive) cavity. The radiated power coupled from the receive cavity is in turn measured with a superheterodyne receiver. In TESR work it is most usual to combine the microwave field emanating from the receive cavity with a strong coherent reference field taken as some suitable fraction of the incident power. The detected output of the superheterodyne receiver is proportional to that component of the transmitted field projected upon the strong reference. The dc magnetic field dependence of this component is termed the signal. The phase of the reference field is made adjustable and by trial and error is adjusted such that the signal is either symmetric or anti-symmetric. If the signal is symmetrized, for example, the centre field value combined with the known driving frequency may be used to calculate a $g$-value, and the width of the resonance signal may be interpreted as a relaxation time. For a Lorentzian response, the full width at half amplitude, $\Delta H$, is related to the experimentally deduced transverse spin relaxation time $T_2^*$ by $\Delta H = \frac{2}{\gamma T_2^*}$, where $\gamma$ is the gyromagnetic ratio [27, 28].

The microwave cavities and sample are located inside suitable Dewars which allow for operation in liquid helium, or in the vapour. Temperatures are monitored utilizing calibrated carbon resistors. The magnetic field is supplied by a Varian 12" magnet equipped with a field-dial control.

### 2.2 SAMPLE PREPARATION

All samples were made by successive dilution from a master alloy incorporating pure ASARCO 5-9 copper. Samples of approximately 10 g weight were melted in a graphite crucible using an rf induction coil located inside a diffusion pumped bell jar. Care was taken to prevent oxidation of the constituents [29], or their evaporation at high temperature. After achieving temperatures for melting, a single crystal was grown via the Bridgman technique. The initial recrystallization was achieved in approximately 10 s, followed by a slow cool down. In general, this procedure produced a single crystal when the alloys contained 300 ppm or less of impurity [30]. The crystals were cut (at random orientations) by a wire spark discharge process and then etched and chemically lapped. The concentrations of impurities were determined by methods listed in table II. All impurity concentrations are known to ± 10 % except for Cr which is ± 5 %. In general there was fair agreement when different methods of analysis were used, however, if systematic difference existed the value retained here was that from resistivity ratio, as it selects only the isolated impurities.

## 3. Experimental measurements

### 3.1 LINENWIDTH DATA

The primary data for any sample consisted of a measurement of the symmetrized resonance linewidth at half maximum, $\Delta H$, at low temperatures. In figure 1, we present a typical set of such data for $\Delta H$ for a CuZn (35 ppm) alloy. The rapid increase in $\Delta H$ above 20 K in both samples is attributed to phonon relaxation and agrees with previous detailed measurements [13, 31]. There is a definite shallow minimum to the linewidth at ≈ 16 K, and this effect is found in most of the alloy samples, as well as the «pure» host material that has not been oxygen treated. We believe the origin for this behaviour is due to a small amount of local moment impurity (most probably Fe) at the fractional ppm level as exemplified in our previous studies of CuCr [15] and by the detailed study of CuFe [10].

In an effort to reduce the residual linewidth and the effects of such unknown local moment impurity, we considered first oxygen treating the host material and then making the various alloys. Unfortunately, we found that upon remelting and crystal growth following the oxygen anneal procedure, the residual linewidth of the pure host material would not remain at the oxygen treated level. Since the unannealed material had rather reproducible behaviour, and since the shallow minimum in $\Delta H$ was not a limiting factor in determining the overall errors of the quantities of interest, we established a procedure whereby the average $\Delta H$ over the temperature range 1.5-20 K was used to characterize the mean residual line-
width of any given alloy. In figures 2a and 2b, this quantity, as just defined, is shown plotted as a function of alloy concentration for seven non-magnetic impurities: Li, Zn, Ga, Ge, As, Ni, and Ti.

Table III.—Spin-flip scattering and resistivity of s + p impurities in copper.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Valence diff.</th>
<th>Spin-orbit constant $\lambda$ (eV)</th>
<th>$\Delta H/\Delta c$ (Gauss/ppm)</th>
<th>$\sigma_{sf}$ (cm$^2$)</th>
<th>$\sigma_{sf}$ theory (cm$^2$)</th>
<th>$\Delta \rho$ ((\mu\Omega\cdot\text{cm}/%))</th>
<th>$\sigma_r$ (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0</td>
<td>(*)</td>
<td>0.26 ± 0.06</td>
<td>1.7 x 10$^{-19}$</td>
<td>0.7 x 10$^{-19}$</td>
<td>0.63</td>
<td>1.1 x 10$^{-16}$</td>
</tr>
<tr>
<td>Zn</td>
<td>1</td>
<td>$4.8 \times 10^{-2}$</td>
<td>0.175 ± 0.025</td>
<td>1.18 x 10$^{-19}$</td>
<td>7.5 x 10$^{-19}$</td>
<td>0.33</td>
<td>1.9 x 10$^{-16}$</td>
</tr>
<tr>
<td>Ga</td>
<td>2</td>
<td>$6.8 \times 10^{-2}$</td>
<td>0.37 ± 0.05</td>
<td>2.5 x 10$^{-19}$</td>
<td>4.8 x 10$^{-19}$</td>
<td>1.7 x 10$^{-19}$</td>
<td>3.8 x 10$^{-16}$</td>
</tr>
<tr>
<td>Ge</td>
<td>3</td>
<td>$1.18 \times 10^{-1}$</td>
<td>0.80 ± 0.1</td>
<td>5.2 x 10$^{-19}$</td>
<td>1.5 x 10$^{-19}$</td>
<td>1.5 x 10$^{-19}$</td>
<td>11.5 x 10$^{-16}$</td>
</tr>
<tr>
<td>As</td>
<td>4</td>
<td>$2.08 \times 10^{-1}$</td>
<td>1.3 ± 0.2</td>
<td>8.7 x 10$^{-19}$</td>
<td>6.5 x 10$^{-19}$</td>
<td>6.8</td>
<td>13.4 x 10$^{-16}$</td>
</tr>
<tr>
<td>Au</td>
<td>0</td>
<td>$6.1 \times 10^{-1}$ (*)</td>
<td>18 ± 6</td>
<td>$1.2 \times 10^{-17}$ (*)</td>
<td>$5.9 \times 10^{-17}$</td>
<td>0.55</td>
<td>0.98 x 10$^{-16}$</td>
</tr>
</tbody>
</table>

(*) From reference [13], $\lambda_{3d}(Au) = 2/5$ spin-orbit splitting of the 5d atomic level.
(\(*\) $\lambda_{p}$ from reference [3] = 2/3 spin-orbit splitting of the p atomic level.
(\(*) Experimental full linewidth increment (this work) except Au is taken from reference [13].
(\(\dagger\) Spin-flip cross-section, exp. (2). The accuracy is that with which $\Delta H/\Delta c$ is determined.
(\(\ddagger\) Resistivity increment for impurities in Cu (experimental) per at. \% Li: this work.
(\(\ddagger\) We take the spin-orbit value for Cu: $\lambda_{3d} = 2.1 \times 10^{-3}$ eV, reference [3].
(\(\ddagger\) Resistivity cross-section from exp. (1).
Table IV. — Spin-flip scattering and resistivity by 3d impurities in copper.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>ΔZ</th>
<th>Z_1</th>
<th>Z_2</th>
<th>λ</th>
<th>ΔH/Δc exp.</th>
<th>σ_{st} exp.</th>
<th>σ_r Th. Eq. (11)</th>
<th>σ_{st} Th. Eq. (8)</th>
<th>Δρ exp.</th>
<th>σ_r exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>45</td>
<td>8.3 x 10^{-2}</td>
<td>5.1 ± 0.4</td>
<td>3.4 x 10^{-18}</td>
<td>1.7 x 10^{-18}</td>
<td>1.7 x 10^{-18}</td>
<td>1.25</td>
<td>2.2 x 10^{-16}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>24</td>
<td>6.7 x 10^{-2}</td>
<td>78 ± ?</td>
<td>5.2 x 10^{-17}(*)</td>
<td>1.5 x 10^{-17}</td>
<td>1.5 x 10^{-17}</td>
<td>7</td>
<td>1.25 x 10^{-15}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>35</td>
<td>2.3 x 10^{-2}</td>
<td>27 ± 16</td>
<td>1.8 x 10^{-17}***</td>
<td>5.2 x 10^{-17}</td>
<td>3.1 x 10^{-17}</td>
<td>9</td>
<td>1.6 x 10^{-15}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>45</td>
<td>1.4 x 10^{-2}</td>
<td>1.9 ± 0.2</td>
<td>5.4 ± 0.5</td>
<td>2.3 x 10^{-18}</td>
<td>3.3 x 10^{-18}</td>
<td>8</td>
<td>1.4 x 10^{-14}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>54</td>
<td>3.2 x 10^{-2}</td>
<td>5.4 ± 0.5</td>
<td>3.6 ± 10^{-18}</td>
<td>1.2 x 10^{-17}</td>
<td>1.2 x 10^{-17}</td>
<td>—</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>62</td>
<td>2.3 x 10^{-2}</td>
<td>5.4 ± 0.5</td>
<td>3.6 ± 10^{-18}</td>
<td>2.8 x 10^{-18}</td>
<td>2.8 x 10^{-18}</td>
<td>10</td>
<td>1.77 x 10^{-15}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>71</td>
<td>1.5 x 10^{-2}</td>
<td>2.7 ± 0.3</td>
<td>1.8 ± 10^{-18}</td>
<td>1.2 x 10^{-17}</td>
<td>1.2 x 10^{-17}</td>
<td>—</td>
<td>—</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(†) Full linewidth from references [7, 10, 13] or present work, see figures 2a and 2b.
(‡) Spin-flip cross-section from equation (2). The accuracy is that with which ΔH/Δc is determined.
(§) Theoretical model, equation (11), simplified from reference [36]. Δd = 0.5 eV everywhere.
(¶) Theoretical model, equation (8), from MONOD, P., These, Université Paris-Sud, Orsay (1968), unpublished. Δ = 0.5 eV.
(*) Resistivity increment in Cu (experimental) per at. % impurity.
(†) Resistivity cross-section from equation (1).
(§) Reference [7].
(‡) Reference [10].
(¶) Reference [13].

The difference in linewidth between a given alloy sample and the pure host is attributed to the increased spin relaxation due to the added impurity. In all cases the impurity concentrations used were within the known limits of solid solubility, and consequently one would expect a linear relationship with the intercept at zero concentration corresponding to the residual linewidth in the pure host Cu. Within the limits of error, this relationship is observed and represented by the solid lines in figures 2a-2b. The incremental linewidth per impurity concentration (i.e., the slope of the lines) is the primary quantity of interest measured in this work. The values of the slopes of the lines for the seven alloy systems studied is presented in table III and table IV along with other quantities pertinent to the discussion of these data in section 4.

3.2 g-VALUE DATA. — The magnetic field at the centre of the symmetrized line in conjunction with the known microwave frequency allows calculation of the g-value of the resonance. Although the addition of impurities may, in principle, produce a g-shift, this shift must be compared to the increase in linewidth to ascertain whether it should be observable in practice [32]. We find that within the limits of error there are no discernable g-shifts either with impurity concentration or temperature over the range 1.5-20 K. The g-value of 2.033 ± 0.001 observed for many alloys agrees with the known pure copper g-value [13, 31].

3.3 INCREMENTAL RESISTIVITY. — In section 2 we noted that in some cases we made use of the known incremental resistivities to determine the impurity concentration of the alloys. For all the alloys except CuLi such values were in the literature. For CuLi we find from our resistivity measurement and our separate chemical analysis that:

\[ \Delta \rho/\Delta c = 0.63 \pm 0.03 \, \mu\Omega \cdot \text{cm/At \%} \]

for Li dissolved in Cu.

4. Discussion. — The specific impurity linewidth broadening may be converted to a spin-flip cross-section \( \sigma_{sf} \) in the same manner as is done for the scattering cross-section \( \sigma_r \) from the resistivity increment \( \Delta \rho/\Delta c \) [33]:

\[ \sigma_r = \frac{1}{N_0 v_F} \frac{d(1/\tau)}{dc} = 1.79 \times 10^{-16} \frac{\Delta \rho}{\Delta c} \frac{1}{\text{cm}^2} \]  

(1)

where \( \rho \) is in \( \mu\Omega \cdot \text{cm} \) and \( c \) is atomic \% \( 1/\tau \) is the collision rate, \( N_0 \) is the number of atoms per \( \text{cm}^3 \) of the host metal and \( v_F \) the Fermi velocity. For the spin-flip cross-section, we have [33]:

\[ \sigma_{sf} = \frac{1}{N_0 v_F} \frac{d(1/T_2)}{dc} = \frac{1}{N_0 v_F} \frac{\gamma \, d\Delta H}{dc} = 0.67 \times 10^{-18} \frac{d\Delta H}{dc} \frac{1}{\text{cm}^2} \]  

(2)
where $\gamma$ is the gyromagnetic ratio and $d\Delta H/dc$ is the slope of the full linewidth versus concentration (in gauss per ppm) as presented in figure 2. The values of $\sigma_{d}$ and $\sigma_{s}$, so deduced, together with values for other impurities previously measured by related methods, are presented in table III (non-transition metal impurities) and table IV (transition metal impurities).

In order to get approximate expressions for the spin-flip cross-section of s-p or d types of impurities in copper, we follow the formulation of Asik, et al. [5], Ferrell and Prange [34], and Yafet [35, 36]. Assuming a single phase shift and a Lorentzian shape curve for the density of state versus energy of width $\Delta$, the spin-flip cross-section is [35]:

$$\sigma_{sf}(d) = \frac{40 \pi}{k_{F}^{2}} \left( \frac{\lambda_{d}}{\Delta_{d}} \right)^{2} \sin^{4} \eta_{d}$$

(3)

$$\sigma_{sf}(d) = 6.80 \times 10^{-15} \left( \frac{\lambda_{d}}{\Delta_{d}} \right)^{2} \sin^{4} \eta_{d} \text{ (cm}^{2} \text{)} \quad \text{(for copper)}$$

for non-magnetic impurities where $\lambda_{d}$ is the d spin-orbit constant, and $\Delta_{d}$ the width of the d virtual bound state ($k_{F}$ is the Fermi momentum of copper). For s + p impurities, we have [35]:

$$\sigma_{sf}(s + p) = \frac{8 \pi}{k_{F}^{2}} \left( \frac{\lambda_{p}}{\Delta_{p}} \right)^{2} \sin^{4} \eta_{s+p} = 1.36 \times 10^{-15} \left( \frac{\lambda_{p}}{\Delta_{p}} \right)^{2} \sin^{4} \eta_{p} \quad \text{(for copper)}$$

(4)

where $\lambda_{p}$ is now the p spin-orbit constant, and $\Delta_{p}$ the width of the s + p virtual bound state. The phase shift is related to the valence difference between the impurity and the host metal by the Friedel sum rule, and assuming only one phase shift to be important. We have:

$$\eta_{d} = \frac{\Delta Z}{10}$$

(5)

$$\eta_{s+p} = \frac{\Delta Z}{8}$$

(6)

in the latter case we have assumed a complete s + p mixing [37] so that $\eta_{0} = \eta_{1}$. In this manner expressions (3) and (4) contain only one parameter, namely, the width of the virtual bound state. This was taken to be 0.5 eV for the transition series and 3 eV for the sp series. The corresponding values for $\lambda$ and $\Delta Z$ are listed in table III and table IV together with relevant parameters to the resistivity.

A special case must be made when the impurity is magnetic, just as the evaluation of the resistivity [38]. At first one may be tempted to treat the spin-flip scattering on a local moment the same way as for the resistivity and write that the spin-flip cross-section is the sum of the cross-section on $d \uparrow$ and $d \downarrow$ electrons forming the virtual bound state [38]:

$$\sigma_{sf} = \sigma_{d\uparrow} + \sigma_{d\downarrow}$$

(7)

which leads immediately to:

$$\sigma_{sf} = \frac{20 \pi}{k_{F}^{2}} \left( \frac{\lambda_{d}}{\Delta_{d}} \right)^{2} (\sin^{4} \eta_{1} + \sin^{4} \eta_{1})$$

(8)

which seems a straightforward extension of (3) with:

$$\eta_{1} = \frac{\pi}{3} Z_{1} \quad \text{and} \quad \eta_{1} = \frac{\pi}{3} Z_{1}$$

(9)

and:

$$Z_{1} + Z_{1} + \Delta Z = 10; \quad \text{(10)}$$

$$\mu_{B}(Z_{1} - Z_{1}) = \text{magnetic moment of the impurity}.$$  

This simple approach has been shown to be incorrect by Yafet [36], as it does not take into account the fact that in the magnetic case the spin-orbit interaction acts on states which are already separated by the Coulomb repulsion and exchange. His complete expression [36] is, however, difficult to handle as it introduces three different spin-orbit enhancement factors. We remark that, as these factors will always appear in a ratio with the state width $\Delta_{d}$, which itself is not well known, it is possible to assume that these factors are identical and retain as a single parameter the quantity ($\lambda_{d}/\Delta_{d}$). With this drastic simplification, we write Yafet’s expression [36] as:

$$\sigma_{sf} = \frac{10}{3} \frac{\pi}{k_{F}^{2}} \left( \frac{\lambda_{d}}{\Delta_{d}} \right)^{2} \times$$

$$\times (2 \sin^{2} \eta_{1} \sin^{2} \eta_{1}(3 + 2 \cos^{2}(\eta_{1} - \eta_{1}))$$

$$+ \sin^{8} \eta_{1} + \sin^{4} \eta_{1})$$

(11)

with the same notation as defined by equation (9) and equation (10). It is apparent that equation (11) cannot be put into a separate sum of $\uparrow$ and $\downarrow$ cross-sections, but does reduce to the simple form of equation (3) if $\eta_{1} = \eta_{1}$. We have evaluated equation (11) and also equation (8), (although incorrect in principle), in table IV. These values appear in figure 3 as a continuous line for equation (11) and a dotted line for equation (8). The main difference between these two occurs whenever one of the phase shifts is zero.
Fig. 3. — Spin-flip cross-sections, \( \sigma_{sf} \), (lower part) and resistivity cross-sections (triangles \( \Delta \), upper part) for transition impurities and s-p impurities in Cu.

### Experimental Values

- Continuous line — Eq. (11) from Ref. [36] theory for 3d impurities.
- Dotted line — Eq. (8) impurities.

When considering the overall pattern of cross-sections presented in figure 3 several points are worthy of attention. First the order of magnitude of the measured spin-flip cross-sections is larger for the transition elements than for the s-p impurities. Second, a monotonic increase is observed between Zn and As while no such behaviour is found in the 3d elements. The spin-flip cross-section tends to follow the pattern known for the resistivity cross-section, that is, with a minimum at Mn. This is, of course, what can be expected from the resonance model since: (1) the ratio \( \lambda/\Delta \) is larger for d impurities than for the s-p type, (2) there is a minimum in the density of d state for Mn. The general agreement is also much better with the d series than that for s-p (see tables III and IV). In this latter respect we note that the Ferrell and Prange method is a two parameter fit (namely the width and the position of the centre of the resonance) leaving unchanged the spin-orbit potential through a series. We have preferred for the sake of comparison to treat both s-p and d elements on the same footing, that is, only choosing a width and requiring that the resonance be fixed by the screening condition. We have then taken the atomic d and p value for \( \lambda \) for each element. No doubt better agreement could be reached by refining the method of fit, but at the expense of losing the possibility to simply compare s-p and d behaviours. Concerning the comparison of equations (8) and (11), the results shown in figure 3 seem to indicate that equation (8), although basically too naive, does not give a worse agreement with Cr, Mn, and Fe than equation (11), although in principle, the latter is more correct. We note that an enhancement of \( \lambda_d \) by a factor of 2 for these 3 elements would result in very satisfactory agreement of the data with equation (11). The major discrepancy occurs for Co: it should be stressed that the data of references [7] and [17] are very tentative, that is why they are only present on figure 3 within parenthesis and no error bars. In the case of Fe the careful analysis of Ritter and Silsbee [10] lead to a spin-flip cross-section notably lower than that roughly indicated by references [7] and [17].

More elaborate calculations of \( \lambda_d \) have been performed for Ni, Zn, Ga, Ge, and Au by Holzwarth and Lee [39]. In their analysis they conclude that their values for Ni and Zn should not be expected to be in close agreement with the data, (and they are not), but their values for Ge and Ga when they include the effects of backscattering by the host agree with our measurements to within the \( \pm 10\% \) error. There is a very substantial disagreement (by a factor \( \approx 3 \)) for Au, and it would suggest that further experimental work for very large spin-orbit impurities is called for.

Finally, special attention should be paid to the Li spin-flip cross-section, specifically to answer the question concerning the importance of spin-orbit coupling in the host. This is best analysed in terms of perturbation theory since in this case since the scattering is expected to be weak and no phase shift would be near \( \pi/2 \). The perturbing potential is now the difference between the spin-orbit potential seen by the conduction electron on the copper lattice and that on the lithium atom. Within this level of approximation the spin-flip scattering cross-section for Li in Cu is expected to be the same as for Cu dissolved in Li, and is expressed conveniently by the formula derived by Asik, et al. [5] via perturbation theory:

\[
\sigma_{sf}(Li\text{Cu}) = \frac{3}{\hbar} \frac{1}{N_0 v_F} \left< \frac{\lambda_0^2}{\epsilon_F}(Cu) \right> \tag{12}
\]

where \( v_F \) is the Fermi energy of Cu and \( \left< \frac{\lambda_0^2}{\epsilon_F}(Cu) \right> \) is the spin-orbit matrix element between wavefunctions conveniently orthogonalized to the core electrons. As is well known, the orthogonalization enhances the amplitude of the wavefunction near the centre of the atom where the spin-orbit potential is strongest. As is shown by Asik, et al. [5], a direct consequence of this is the \( \Delta Z^2 \) valence effect on \( \sigma_{sp} \). The same argument, of course, applies for the resistivity in dilute alloys of increasing valence difference. Figure 4 is a display of such a valence effect through
The valence effect on the «spin-orbit hole» spin-flip cross-section of a light impurity in Cu compared to heavier impurities next to Cu in atomic weight. The $\Delta Z^2$ dependence simply follows from perturbation as noted by Asik, et al. [5]. The sources of the data are presented in Table I.

The series Zn, Ge, and As, already discussed, and the series Li, Mg, Al, Si. It is most remarkable that these elements with negligible spin-orbit (compared to Cu) give a larger spin-flip cross-section than the Zn, Ga, Ge, As series. From this fact, it is clearly apparent that it is the spin-orbit difference between the impurity and the host that is the relevant parameter for $\sigma_d$ [40].

5. Conclusions. — We have presented an experimental determination of the spin-flip cross-section for non-magnetic and magnetic impurities in copper obtained from the direct measurement of the rate of increase of the conduction electron spin resonance linewidth with concentrations of these impurities. We have used a simple set of expressions derived from a virtual bound state model to estimate the spin-flip cross-sections of transition 3d impurities. For non-transition (s-p) impurities, we estimate the spin-flip cross-section following the perturbation approach of Asik, et al. [5]. Although many of these individual estimates might certainly be refined, we note that the general variation of the experimental spin-flip cross-section, which cover nearly three orders of magnitude, are satisfactorily accounted for by our elementary analysis.

Acknowledgments. — We gratefully acknowledge helpful discussions with Y. Yafet, J. Friedel, and M. R. Shanabarger. We thank M. R. Shanabarger for communicating to us his unpublished data for Au, and H. Hurdequint for his data on Sb and Cr.

References

    $\sigma_d(Mn_{\text{in AgMn}}) = (1.75 \pm 0.2).10^{-18}\text{cm}^2$
    $\sigma_d(Au_{\text{in Cu}}) : \text{see table III.}$
[19] COTTET, J., Thèse Université de Genève (1970) unpublished, and private communication : from the analysis of CuMn 1% we get :
    $\sigma_d(Pd) = (2.5 \pm 0.5).10^{-18}\text{cm}^2$
    $\sigma_d(Au) = (2 \pm 0.4).10^{-17}\text{cm}^2$ (See Fig. III)
    $\sigma_d(Pt) = (4 \pm 1).10^{-17}\text{cm}^2$. 

5. Conclusions. — We have presented an experimental determination of the spin-flip cross-section for non-magnetic and magnetic impurities in copper obtained from the direct measurement of the rate of increase of the conduction electron spin resonance linewidth with concentrations of these impurities. We have used a simple set of expressions derived from a virtual bound state model to estimate the spin-flip cross-sections of transition 3d impurities. For non-transition (s-p) impurities, we estimate the spin-flip cross-section following the perturbation approach of Asik, et al. [5]. Although many of these individual estimates might certainly be refined, we note that the general variation of the experimental spin-flip cross-section, which cover nearly three orders of magnitude, are satisfactorily accounted for by our elementary analysis.

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References
[21] Hurdé Quint, H., private communication:
\[ \sigma_{\text{sf}}(\text{Sb in AgSb}) = (8.8 \pm 1) \times 10^{-18} \text{ cm}^2 \]
\[ \sigma_{\text{sf}}(\text{Cr in AgCr}) = (4 \pm 2) \times 10^{-18} \text{ cm}^2. \]
The microscopic mechanism of this effect has been investigated by Fert, A. and Levy, P. M., Phys. Rev. Lett. 44 (1980) 1538.
[30] As copper is cubic, one does not expect the spin-flip cross-section to depend on crystal orientation, at least for spherically symmetric impurities, so the requirement for single crystal was only practical in order to have a very homogeneous chemical polish necessary to achieve sample thickness down to 25 \( \mu \text{m} \) or less.
[33] This definition is equivalent to that of Asik (Ref. [5]) and corresponds to the cross-section calculated by Yafet [35] as noted in reference [6]. The coefficients are calculated from the tabulated parameters of Cu in Ashcroft, N. W. and Mermin, N. D., Solid State Physics, Holt, Rinehart and Winston Eds. (1970) and with \( g(Cu) = 2.033. \)
This formulation implies that the spin-orbit perturbation is due primarily to the p or d valence electrons rather than the core ones. This is indeed a valid assumption as can be seen from table II, p. 80, of reference [3] where the spin-orbit splittings of each atomic level is given together with the energy difference of that level with the valence state. By forming the ratio of these two quantities for each level one measures the strength of the spin-orbit perturbation of the valence electron by that level. For all cases one find a largest contribution for the p or d level immediately below the valence electrons.
The definition of spin-flip cross-section in this paper is one-half of that defined in [35] and so corresponds to one-half of the definition used in references [5] and [6], and equation (2).
[38] Daniel, E. and Friedel, J., Low Temperature Conf. LT9, Columbus, Ohio (1964); Kittel, C., Quantum Theory of Solids, Ch. 18 (John Wiley & Sons, Inc., New York) 1963.
[40] As noticed by H. Hurdé Quint (private communication) there seems to be an apparent contradiction between the \( \Delta Z^2 \) dependence derived from the simple perturbation arguments of Asik, et al. (§ II D of Ref. [3]) and the \( \Delta Z^4 \) prediction obtained from expression (4) in the limit of small phase shift where this expression is expected to coincide with that of perturbation. As shown by Yafet [35] the spin-flip cross-section depends upon the square of the density of state of the screening electrons. This is consistent with the perturbation approach, however the valence effect in that case enters only via the orthogonalization coefficients of the wavefunction to the core electrons without affecting the remaining density of state factor. It should be noticed that this latter analysis seems to be in good agreement with our observation in copper, but, of course, is expected to breakdown when the phase shifts are no longer small.