Direct relaxation of a local moment spin to the lattice

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DIRECT RELAXATION OF A LOCAL MOMENT SPIN TO THE LATTICE

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ABSTRACT

Two new relaxation processes of a localized spin moment in a metal are considered: A one-step process in which the local spin is flipped while a conduction electron is scattered without flipping its spin, and a two-step process involving first a change in a local moment by two $\hbar$ units, and subsequently an exchange scattering which flips another local moment by $\hbar$ in the opposite direction. Both processes occur in third order of perturbation theory under the combined action of *s-d* mixing and spin-orbit interaction. The calculated values of the relaxation time for *Mn* and *Cr* in *Cu* are in good agreement with the measured values.

Measurements [1, 2] of the resonance linewidth in solutions of 3*d* local moments in the noble metals have provided experimental values for the relaxation time T_2 in the bottlenecked regime. Given the fact that the g values of these local moments are very close to the g value of the host conduction electrons, Hasegawa's equations [3] predict that at low concentration the spin-lattice relaxation time T_1, which determines the rate of loss of Zeeman energy by the spin system, is very nearly equal to the linewidth T_2.

Previous discussions of the spin-lattice relaxation have been confined to a two-step process in which, first, the local moment and a conduction electron mutually flip their spins under the effect of exchange (T_{sd} and T_{ds} being the corresponding spin-flip times) and second, the conduction electron spin relaxes with a characteristic time T_{sl} to the energy reservoir provided by the kinetic energy of the conduction electrons. This second step occurs under the influence of the spin-orbit interaction. When the system is bottlenecked ($T_{sl} \gg T_{sd}$) and when the local moment susceptibility dominates over the Pauli susceptibility, the effective spin-lattice relaxation time resulting from this process is

$$\frac{1}{T_{eff}} = \frac{T_{sd}}{T_{ds}} \frac{1}{T_{sl}} \tag{1}$$

In this note [4] we point out the existence of two alternative relaxation processes which do not involve the time T_{sl}, namely process 1: The local moment spin flips by one $\hbar$ unit, the Zeeman energy being transferred in a single process to the kinetic energy of a conduction electron *without* involving a change in the latter's spin, and process 2: Which is a two-step process, first the local moment spin flips by two $\hbar$ units while a conduction electron is scattered with a change in its own spin in the opposite direction, and second, the conduction electron restores its spin to the original direction by exchange-scattering against another local moment. The net change in the local moment spin system is thus one $\hbar$ unit.

Both processes 1 and 2 occur in third order of perturbation theory under the combined action of the *s-d* mixing and the spin-orbit interaction. Denoting by $T^{(1)}_{dl}$ and $T^{(2)}_{dl}$ the corresponding spin-lattice times, the total relaxation rate is

$$\frac{1}{T_1} = \frac{1}{T_{eff}} + \frac{1}{T^{(1)}_{dl}} + \frac{1}{T^{(2)}_{dl}} \tag{2}$$

and is to be compared with the experimental linewidth. The orbital moment is assumed quenched here so that all the relaxation proceeds via the spin-orbit coupling.

Experimentally [1], a temperature independent contribution to the linewidth has been observed. The times $T^{(1)}_{dl}$ and $T^{(2)}_{dl}$ depend on temperature as T^{-1} so that they are not related to any temperature-independent broadening and the interpretation of the latter is still open. An outline of the calculation of $T^{(1)}_{dl}$ and $T^{(2)}_{dl}$ follows.

The system is described by the Anderson hamiltonian including the conduction band energy H_s, the full energy of the 3*d* ion, H_d (including the electron-electron interaction), the *s-d* mixing interaction H_{sd}, and the spin-orbit interaction H_{so}. The unperturbed hamiltonian is $\mathscr{H}_o = H_s + H_d$ and the perturbation is $\mathscr{H}' = H_{sd} + H_{so}$. Since we require orbital quenching of the localized state, our calculation will be valid for an *S* state of H_d; if we were to include crystal field effects we could also treat orbital singlets [5]. Here we deal only with the *S* state case so that our calculation is applicable to *Mn* in the noble metals in the limit where the level width is small compared to the Coulomb energy.

a. *Calculation of* $T^{(1)}_{dl}$. Let $|\,{}^6S_m>$, where $m = -5/2$ to $+5/2$, denote the state of the local moment and let $|\,\underset{\sim}{k}\,\underset{\sim}{\sigma}>$ denote the conduction electrons states. We are interested in transitions that flip the local spin alone, i.e. transitions from the initial state $|\,{}^6S_m>|\,\underset{\sim}{k}\,\underset{\sim}{\sigma}> \;\equiv\; |\,m, \underset{\sim}{k}\,\underset{\sim}{\sigma}>$ to the final state $|\,m \pm 1, \underset{\sim}{k'}\,\underset{\sim}{\sigma}>$. These transitions occur in third order of H', with H_{sd} acting twice and H_{so} acting once. For instance, a conduction electron $|\,\underset{\sim}{k}\,\underset{\sim}{\sigma}>$ jumps (by H_{sd}) onto the impurity, then one of the electrons on the impurity flips its spin (H_{so}) and finally one of the electrons on the impurity comes off (H_{sd}) with the same spin as the incident electron and goes into the conduction band state $|\,\underset{\sim}{k'}\,\underset{\sim}{\sigma}>$. The matrix element for this transition is:

$$M(m-1, \underset{\sim}{k}'\sigma; m, \underset{\sim}{k}\sigma) = \sum_{r,s} \frac{\langle m - 1, \underset{\sim}{k}'\sigma \mid H' \mid r\rangle\langle r \mid H' \mid s\rangle\langle s \mid H' \mid m, \underset{\sim}{k}\sigma\rangle}{(E(m, \underset{\sim}{k}\sigma) - E_r((E(m, \underset{\sim}{k}\sigma) - E_s)} \tag{3}$$

where the sum is over all possible intermediate states. It is sufficient to compute the $m \rightarrow m - 1$ transitions since the $m \rightarrow m + 1$ transitions can then be obtained by time reversal.

There are three types of terms in Eq. (3) corresponding to the three possible positions of H_{so} in the product of factors. Note that if H_{so} is at the right or left positions it acts on the ^6S, $j = 5/2$ state and gives [6] a ^4P, $j = 5/2$ state which, having the same number of electrons as the ^6S state, is separated from the latter by an exchange energy $\mathcal{J}$. In terms of the Slater integrals F^2 and F^4 for the free ion, $\mathcal{J}$ has the value [6]

$$\mathcal{J} = \frac{1}{7}F^2 + \frac{10}{21}F^4 \tag{4}$$

On the other hand if H_{so} is in the middle position, H_{sd} acting on the ^6S state changes the number of d electrons by ± 1 so that the corresponding excitation energies are U_+, the energy needed to promote an electron from the Fermi level to the local moment, and U_-, the energy needed to promote an electron from the local moment to the Fermi level.

The transition rate from $|m\rangle$ to $|m - 1\rangle$ is given by

$$W_{m-1,m} = \frac{2\pi}{\hbar} \sum_{\sigma} \langle \mid M(m-1, \underset{\sim}{k}'\sigma; m, \underset{\sim}{k}\sigma) \mid^2 \rangle_{\underset{\sim}{k},\underset{\sim}{k}'} (N\rho_{at}(\varepsilon_F))^2 k_B T \tag{5}$$

where $\langle\ \rangle_{\underset{\sim}{k},\underset{\sim}{k}'}$ denotes the average over $\underset{\sim}{k}$ and $\underset{\sim}{k}'$ at the Fermi sphere (free electron conduction band), $\rho_{at}(\varepsilon_F)$ is the density of conduction band states at the Fermi level per atom, for one spin direction, and N is the number of atoms in the crystal.

The spin-lattice relaxation rate is [7]

$$\frac{1}{T^{(1)}_{dl}} = 2\frac{\sum_m W_{m-1,m}(E_m - E_{m-1})^2}{2\sum_m E_m^2} \tag{6}$$

where the factor 2 takes into account the transitions $m \rightarrow m + 1$. We omit the details of the calculation of $W_{m-1,m}$, which will be published in a more comprehensive paper, and give only the final result. Defining the quantity C,

$$C = \frac{2}{\pi\hbar}\lambda^2\Delta^2 k_B T \tag{7}$$

where λ is the spin-orbit constant of the $3d$ state, and Δ the virtual level width, which is proportional to the square of the s-d mixing interaction, we find for the relaxation rate:

$$\frac{1}{T^{(1)}_{dl}} = \frac{C}{25}\left[7\left(\frac{1}{U_+^2} + \frac{1}{U_-^2}\right)^2 - \frac{20}{U_+^2 U_-^2} + \frac{8}{\mathcal{J}^2}\left(\frac{1}{U_+} + \frac{1}{U_-}\right)^2 + \frac{8}{\mathcal{J}}\left(\frac{1}{U_+} + \frac{1}{U_-}\right)\left(\frac{1}{U_+^2} + \frac{1}{U_-^2}\right)\right] \tag{8}$$

b. *Calculation of* $T^{(2)}_{dl}$. The transitions from the state $|m, \underset{\sim}{k}_\downarrow\rangle$ to the state $|m-2, \underset{\sim}{k}'_\uparrow\rangle$ are calculated in the same fashion and the transition rates $W_{m-2,m}$ are given by an expression analogous to Eq. (5). To obtain the corresponding relaxation rate we note that the relaxation process is completed only when the conduction-electron spin is restored to its original value, i.e. after a subsequent transition $|m-2, \underset{\sim}{k}'_\uparrow\rangle \rightarrow |m-1, \underset{\sim}{k}''_\downarrow\rangle$ occurs. Since this transition occurs via the exchange coupling which is large compared to λ, the rate-determining matrix element is $W_{m-2,m}$ but the net change in the Zeeman energy is that of one spin moment instead of two. The relaxation rate is then

$$\frac{1}{T^{(2)}_{dl}} = \frac{1}{4}\frac{\sum_m W_{m-2,m}(E_m - E_{m-2})^2}{\sum_m E_m{}^2} \tag{9}$$

as follows from Eq. (6) for equally spaced spin levels. Making use of the calculated values of $W_{m-2,m}$ we find:

$$\frac{1}{T^{(2)}_{dl}} = \frac{4C}{25}\left[\frac{1}{U_+^2} + \frac{1}{U_-^2} + \frac{2}{J}\left(\frac{1}{U_+} + \frac{1}{U_-}\right)\right]^2 \tag{10}$$

c. *Calculation of* T_{sl}. Even though the calculation of T_{sl} (transitions $|m, \underset{\sim}{k}_\uparrow\rangle \rightarrow |m\,\underset{\sim}{k}'_\uparrow\rangle$) and of the corresponding T_{eff} has previously been done [8] in the Hartree-Fock (*HF*) approximation, we do it over by perturbation theory for purposes of comparison. The matrix element $M(m, \underset{\sim}{k}'_\downarrow; m\,\underset{\sim}{k}_\uparrow)$ is calculated according to Eq. (3) and after averaging over $\underset{\sim}{k}$ and $\underset{\sim}{k}'$ the rate T_{sl}^{-1} (which is proportional to the atomic concentration of $3d$ impurities, c) is found. To compare with the *HF* value of σ_{sf} given in Reference [8] we use the relation $T_{sl}^{-1} = (cv_F/\Omega)\,\sigma_{sf}$ where v_F is the Fermi velocity and Ω the atomic volume. To compare with T_{dl} we use the relation $T_{eff} = T_{sl}\,[2c\,S(S+1)\,/\,3\rho_{at}(\varepsilon_F)\,k_B\,T]$ which follows from Eq. (1).

We find: (1) The value of σ_{sf} calculated from perturbation theory is equal to the limiting value of the *HF* result for small (Δ/U). This limit is obtained by letting $\sin^2\delta_\uparrow \approx \Delta^2/U_-^2$ and $\sin^2\delta_\downarrow \approx \Delta^2/U_+^2$ in the *HF* expression of Reference [8]. Thus the *HF* result, which is valid in the limit $(\Delta/U) \gg 1$, reduces correctly to the perturbation result which is valid in the opposite limit, $(\Delta/U) \ll 1$. (2) The perturbation calculation shows that the enhancement factor $(1-U/_{orb}U_{sp})^{-1}$ relating to $\tilde{\lambda}$, the off-diagonal component of the spin-orbit interaction in Reference [8], owes its origin to those terms in Eq. (3) where H_{so} is at the right or left position in the third order matrix element so that one of the energy denominators in Eq. (3) is $\mathcal{J}$. This is shown by first, verifying that it is these terms which give rise to the partial cross section σ_{od} which depends on $\tilde{\lambda}$ in Reference [8], and second, by examining the limit of σ_{od} when $\Delta \langle\langle U$. This limit is:

$$\sigma_{od} = \frac{4\pi}{k_F^2}\frac{10}{3}\left(\frac{\lambda}{\Delta}\right)^2\left(\frac{U_{sp}}{U_{sp}-U_{orb}}\right)^2\frac{\Delta^4}{U_+^2U_-^2} \tag{11}$$

The quantity U_{sp} is to be identified with $U_+ + U_-$ and the difference $U_{sp} - U_{orb} = (1/7)\,F^2 + (10/21)\,F^4$, calculated from Referncee [8] is precisely equal to $\mathcal{J}$. This identification of the origin of an enhancement factor in the *HF* calculation with a group of terms in the perturbation expansion is illuminating and it provides a satisfactory bridge between the two calculations.

From the calculation of T_{sl}, the following expression for $T_{eff}^{-1} \equiv (T_{sd}/T_{ds})\,T_{sl}^{-1}$ is found:

$$\frac{1}{T_{eff}} = \frac{C}{7}\left[\left(\frac{1}{U_+^2}+\frac{1}{U_-^2}\right)^2 + \frac{8}{\mathcal{J}^2}\left(\frac{1}{U_+}+\frac{1}{U_-}\right)^2\right] \tag{12}$$

where C is the constant given by Eq. (10).

d. *Comparison with Experiment.* Because of the fact that the portion of the linewidth that is proportional to T had previously been thought to arise *exclusively* from the T_{sl} process, all of the temperature-dependent linewidth has been interpreted [1, 2] as a T_{sl} process. However all three processes, T_{sl}, $T_{dl}{}^{(1)}$ and $T_{dl}{}^{(2)}$ give linewidths proportional to T so that only their combined effect given by Eq. (2) is obtained from the temperature-dependent linewidth. Thus the value $1/T_{sl} = 4.8 \times 10^7$ sec^{-1}/ppm deduced [1] for *Cr* in *Cu* is actually an apparent rate, given by the sum $1/T_{app} = 1/T_{sl} + X_r\,(1/T_{dl}^{(1)} + 1/T_{dl}^{(2)})$ where $X_r = (T_{ds}/T_{sd})$. The deduced spin-flip cross section is *not* the true cross section of the impurity for flipping the electron spin but differs from it by a factor R,

$$R = T_{eff}\,/\,T_1 = 1 + X_r\,T_{sl}\,(1/T_{dl}^{(1)} + 1/T_{dl}^{(2)}) \tag{13}$$

which is directly obtainable from Eq's. (8), (10) and (12) when the values of U_+, U_-, and $\mathcal{J}$ are known.

The only S state ion with which we can compare our theory is Mn^{2+}. Shanabarger [2] measured the T dependent part of the width and found $1/\gamma\,(T_2)_{app} = 0.96$ gauss/ppm. The corresponding value of the apparent spin-flip cross section is

$(\sigma_{sf})_{app} = 1.27 \times 10^{-18}\ \mathrm{cm}^2 = R\sigma_{sf}$where σ_{Jf} is the true conduction electron spin-flip cross section.

To calculate σ_{sf} and R we need to know the quantities λ, Δ, U_+, U_-, and $\mathcal{J}$. The value of λ for the $Mn^2{}_+$ ion is [9] $\lambda = 330\ \mathrm{cm}^{-1}$. The value of Δ for Mn in Cu has not been measured, but for Ni in Cu the measured value is [10] $\Delta \simeq 0.3$, and for Ti in Cu, the estimated value is [11] $\Delta = 1.0\ eV$. For Mn, we estimate $\Delta = 0.55\ eV$.

The values of U_+ and U_- are estimated from the measured [12] saturation moment of Mn which is $(n_\uparrow - n_\downarrow)\ \mu_B = 4.0\ \mu_B$ and from the assumed total number of d electrons on Mn in solution, $n_\uparrow + n_\downarrow$, which we estimate to range between 5.0 and 5.4. Use of the Lorentzian approximation for the virtual level gives then the quantities U_+ and U_-. Finally we take $\mathcal{J} = \frac{1}{2}(U_+ + U_-)$ which is a value close to but smaller than the ${}^6S - {}^4P$ separation in the free ion.

With these values of the parameters the three relaxation times T_{sl}, $T^{(1)}_{dl}$, and $T^{(2)}_{dl}$ as well as the corresponding σ_{sf} and the factor R have been calculated. The results are shown in Table 1. It is seen that the calculated σ_{sf} does not vary much as $n_\uparrow + n_\downarrow$ varies between 5.0 and 5.4, even though U_+ and U_- vary appreciably. At fixed $n_\uparrow$ and $n_\downarrow$, if Δ is allowed to change, the resulting σ_{sf} varies as Δ^{-2} and R does not change. This follows since U_+, U_- are proportional to Δ when $n_\uparrow$, $n_\downarrow$ are fixed.

The agreement between the calculated $(\sigma_{sf})_{app}$ and the experimental value of $1.27 \times 10^{-18}\ \mathrm{cm}^2$ is too close to be meaningful since the actual state of the Mn ion is probably not so close to the perturbation limit. Agreement within a factor of 2 should be considered good.

Finally, the case of Cr can be qualitatively compared with the present theory. The measured value is [1] $(\sigma_{sf})_{app} = 3.6 \times 10^{-18}\ \mathrm{cm}^2$ and the value of σ_{sf}, using only the T_{sl} process, and calculated in Hartree-Fock approximation is[8] $2 \times 10^{-18}\ \mathrm{cm}^2$. A factor R between 2 and 3 gives qualitative agreement, but Cr is probably less close to the perturbation limit than Mn, and in any event a separate calculation would have to be made for Cr since it is not in an S state in the ionic limit.

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I am grateful to M. R. Shanabarger for communicating his unpublished measurements and allowing me to quote his result.

TABLE I

Calculated values of $_{sf}$ *and* $(_{sf})_{app} = R_{sf}$ *for Mn in Cu.*

$n\uparrow + n\downarrow$	U_+ [eV]	$U-$ [eV]	$\mathscr{J}$[eV]	$R = \frac{T_{eff}}{T_1}$	σ_{sf} [cm^2	$(\sigma_{sf})_{app}$ [cm^2
5.4	1.46	3.60	2.53	3.12	4.22×10^{-19}	1.32×10^{-18}
5.2	1.74	2.68	2.21	2.77	4.92×10^{-19}	1.36×10^{-18}
5.0	2.12	2.12	2.12	2.68	4.62×10^{-19}	1.24×10^{-18}

The values assumed for the local moment parameter are: $n_\uparrow - n_\downarrow = 4.0$; $\Delta = 0.55\ eV$; and the values of $n_\uparrow + n_\downarrow$ listed in the first column. The values of U_+ and U_- then follow from the virtual level description. $\mathscr{J}$ is taken to be $\frac{1}{2}(U_+ + U_-)$. The measured value of $(\sigma_{sf})_{app}$ is 1.27×10^{-18}cm^2.

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DISCUSSION

MONOD: Is the mechanism by which you have this spin-flip of the local moment and no spin-flip of the conduction electron just like the one that Giovannini calculated in the anomalous Hall effect, and which boils down to a spin-orbit interaction in which it is the spin of the magnetic impurity and the orbit of the conduction electron?

YAFET: If you want, yes.

MONOD: You have an interaction $\lambda^*\ l \cdot S$ which does the same thing as Yafet says.

ORBACH: Is that a spin-other orbit that you are talking about? This I thought was a spin-orbit on the same ion.

GIOVANNINI: This effective interaction can have various sources, and one is the one that has been described by Yafet, which gives the same functional form for the interaction.