Importance of direct Coulomb d-f interaction in the relaxation of 170Yb3+ in palladium

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1. Introduction.

Mössbauer emission spectra of the $^{170}$Yb ion diluted in palladium have been recently measured between 0.11 and 2 K [1]. It was shown that the $\Gamma_7$ doublet is the ground state and that the $\Gamma_8$ quartet is very close to the ground state, while the $\Gamma_6$ doublet is far above $\Gamma_7$. The relaxation rate $1/T_1$ of the ground state $\Gamma_7$ of ytterbium in palladium has been attributed to its coupling with conduction electrons and has been fitted between 0.11 and 2 K by the law:

$$
\frac{1}{T_1} = C_K T [1 + \beta f(\Delta/k_B T)]
$$

(1)

where $f(x) = x/(e^x - 1)$.

In expression (1), $C_K$ represents the coefficient of the Korringa relaxation within the ground state, while the «acceleration coefficient» $\beta$ corresponds to the relaxation towards the excited level $\Gamma_8$ lying at a distance $\Delta$ above the ground state. The best fit to the relaxation rate in the PdYb alloys has been obtained by taking the following set of parameters: $C_K = 120 \pm 20$ MHz/K, $\beta = 4.2 \pm 1.0$ and $\Delta = 2.5 \pm 0.5$ K [1].

With the $\Gamma_8$ quartet lying at 2.5 K from the ground state $\Gamma_7$, one may wonder whether it could be observed out of thermal equilibrium in the Mössbauer emission spectrum at 0.11 K. This implies that the depopulation rate of $\Gamma_8$ towards $\Gamma_7$ be lower than the inverse lifetime $1/2 \pi \tau \approx 68$ MHz of the nuclear excited state of $^{170}$Yb.

With the fitted values for $C_K$, $\beta$ and $\Delta$, we obtain...
The saturation value of the transition probability \( W_{r_8 \rightarrow r_7} \) from \( r_8 \) to \( r_7 \) is, therefore, much greater than \( 1 / L n' \) which means that the \( r_8 \) population reaches Boltzmann equilibrium a long time before the emission of the Mössbauer \( \gamma \)-ray, and so the \( r_8 \) state is unobservable on the spectrum at 0.11 K.

The purpose of the present paper is to re-examine theoretically the problem of relaxation in PdYb alloys, which was already studied in reference [1]. It is well known that, in such dilute alloys with rare-earth impurities, the relaxation of the ground state is due to the coupling of the 4f electrons with conduction electrons. In reference [1] we have already derived the relaxation rate of the ground state \( r_7 \) in PdYb alloys by taking an exchange interaction between 4f and conduction electrons and here we would like to improve the description of reference [1] by considering the direct Coulomb interaction in addition to the exchange interaction.

The « acceleration coefficient » \( \beta \) depends on the type of interaction between 4f localized and conduction electrons. It is equal to \( \beta = 1 \) [2] when one considers the classical isotropic exchange \( s-f \) Hamiltonian between the 4f-spin \( S \) and the spin \( s \) of the s-like conduction electron:

\[
H = - \Gamma S \cdot S .
\]  
(2)

Thus, in a first step, we have tried to account theoretically for the anomalously large value of \( \beta \), by assuming that the relaxation mechanism is due to an atomic exchange interaction between localized 4f electrons of ytterbium and conduction electrons with d character \((l = 2)\) mainly originating from palladium 4d-bands. Using the formalism introduced in reference [3], we have written [1] the d-f atomic exchange Hamiltonian between the 4f-spin \( S \) and the spin \( s \) of the s-like conduction electron:

\[
\mathcal{H}_{d-f} = \sum_{k,m,a} A_{kma}^{d-f} C_k^* C_m^* C_a .
\]  
(3)

In (3), the conduction electrons are described by the operators \( C_{kma} \) (or \( C_{kma}^* \)), where \( |kma\rangle \) is a partial wavefunction of wavenumber \( k = |k| \), with \( l = 2 \), \( m = l \) and spin \( \sigma \). The 4f electrons of ytterbium are described by the operators \( C_s \) (or \( C_s^* \)) where \( |s\rangle \) denotes a 4f-wavefunction in the presence of both spin-orbit coupling and crystalline field.

The calculation of the relaxation rate with the Hamiltonian (3) increases the value of \( \beta \) [1], which is found to be 2, if only the first \( G^1 \) exchange integral is retained and 1.83 when a full calculation is performed including the three \( G^1, G^3 \) and \( G^5 \) d-f exchange integrals and when we take the \( G^3/G^1 \) and \( G^5/G^1 \) ratios equal to the values given by Chow [4]. Note that, in our previous calculation [1], we only considered the relaxation due to \( r_7 \) and \( r_8 \) at an energy \( \Delta \) and neglected the influence of \( r_6 \).

On the other hand, it was recently recognized that the direct Coulomb interaction between 4f and d-conduction electrons is important in explaining the EPR and transport properties of noble metals with rare-earth impurities [5]. Thus, the purpose of the present paper is to include direct Coulomb interaction terms in the derivation of the relaxation rate, in order to see whether it leads to a larger \( \beta \) value.

### 2. Calculation of the relaxation rate.

Now we would like to compute the impurity relaxation rate due to both exchange and direct Coulomb interaction processes within the anisotropic d-f interaction Hamiltonian.

The d-f interaction Hamiltonian can still be formally written as (3) with the interaction constant now given by:

\[
\Delta_{kma}^{d-f} = \Delta_{kma}^{s-f} - \Delta_{kma}^{d-f} .
\]  
(4)

The exchange interaction constant \( \Delta_{kma}^{s-f} \) corresponds to the exchange process and is given by equation (25) of reference [1]. Now we have to compute the direct Coulomb interaction constant \( \Delta_{kma}^{d-f} \).

We use exactly the same formalism as in the beginning of § 6 of reference [1]. The relaxation rate \( 1/T_1 \) is given by (see Eq. (13) of Ref. [1]):

\[
\frac{1}{T_1} = 2 W_{r_7 \rightarrow r_7} + \sum_{i \in r_7} W_{r_7 \rightarrow i} .
\]  
(5)

with the notation of reference [1].

The transition probability \( W_{ag} \) is given by the following equation (similar to the Eq. (15) of Ref. [1]):

\[
W_{ag} = \frac{2 \pi n(E_p)^2}{a} \left[ \frac{\Delta_{ag}}{\hbar(2l + 1)} \right] \cdot \sum_{m'_a} \left( \Delta_{kma}^{s-f} - \Delta_{kma}^{d-f} \right)^2 .
\]  
(6)

where \((2l + 1) = 5\) corresponds to the orbital degeneracy of the d-electrons, \( n(E_p) \) is the density of states for conduction electrons at the Fermi level and \( \Delta_{ag} = E_g - E_a \) is a crystal field splitting.

The first term of (6) corresponding to the exchange processes only has been computed in reference [1] as a function of the three d-f radial exchange integrals \( G^1, G^3 \) and \( G^5 \). We have seen that the « acceleration
coefficient $\beta$ given in (1) is equal to $\beta = 1.83$ when a full calculation including the three $l = 1$, 3 and 5 terms is performed and equal to $\beta = 2$ when only the $l = 1$ exchange integral $G^1$ is considered. Thus, most of the numerical result for $\beta$ is given by the $l = 1$ term. In the following, we will only consider the $G^1$ integral, since it does not deeply modify the final result and since it greatly simplifies the calculations. Within this simplifying approximation, the exchange constants are given by [1]:

$$\sum_{n'} \left| A_{k m n'}^{\text{exchange}} \right|^2 = (3/7)^2 (G^1)^2$$

where $\beta$ denotes the other state of $\Gamma_7$ (labelled $\Gamma_7^\beta$) and any state of $\Gamma_8$.

Now, let us compute the direct Coulomb interaction constants $A_{k m n}^\text{direct}$, which are given by:

$$A_{k m n}^\text{direct} = \langle \chi_d | \phi_{k m n} | 1/r_{12} \rangle \phi_{k m n} \chi_d \rangle$$

where $\chi_d(r)$ is a 4f-wave function corresponding to the crystal field state $\alpha >$ and $\phi_{k m n}$ is an atomic-like wave function for the d-conduction electrons. Each wave function $\chi_d(r)$ is decomposed into a radial part $\theta_d(r)$ and an angular part $\psi_d(Q)$:

$$\chi_d(r) = \theta_d(r) \psi_d(Q)$$

Now, let us recall the main definitions of reference [1] which are necessary for understanding the following:

Each function $\psi_d(Q)$ is a linear combination of two eigenfunctions of $J_z$, i.e.:

$$\psi_d(Q) = \gamma_{s M} \psi_s(Q) + \delta_{s M} \psi_M(Q)$$

$\psi_M(Q)$ has $J_z = M$ as eigenvalue.

Each eigenfunction $\psi_M(Q)$ is then decomposed according to the orbital and spin variables:

$$\psi_M(Q) = \lambda_M Y_{3}^{M+1/2}(Q) X_1 + \mu_M Y_{3}^{M-1/2}(Q) X_1$$

where $Y_{3}^{M}(Q)$ is the spherical harmonic, $X_a$ the spin function, $\lambda_M$ and $\mu_M$ the Clebsch-Gordon coefficients defined by:

$$\lambda_M = \frac{7 - 2M}{14}$$

$$\mu_M = \frac{7 + 2M}{14}$$

The d-conduction electron wavefunction is given by:

$$\phi_{k m n}(r) = R_d(r) Y_7^{m}(Q) X_a$$

where $R_d(r)$ is the radial part.

As in reference [1], we expand $1/r_{12}$ in spherical harmonics. In addition to the three d-f radial exchange integrals $G^l$ given in reference [1], we define here the three d-f Coulomb integrals $F^l$ (with $l$ equal to 2 and 4):

$$F^l = \int dr_1 dr_2 \theta_d(r_1) \theta_d(r_2) R_d(r_2) (r_2/r_1)^{l-1}.$$  

In the following, the coefficients defined by Condon and Shortley [6] for the addition of 3 angular momenta are defined by:

$$C^l(m; m', m'') = \frac{4\pi}{\sqrt{2k + 1}} \times$$

$$\times \int d\Omega (Y^m_l(\Omega))^* Y^{m'-m''}_{k}(\Omega) Y^{m''}_{k}(\Omega).$$

Let us call $M_1$ and $M_2$ the eigenvalues corresponding to the two eigenfunctions which appear in the expansion (10) of the crystal field function $\psi_d(Q)$ and $M_3$ and $M_4$ the two eigenvalues appearing similarly in the expansion of the $\psi_d(Q)$ function.

It results that the non-zero direct Coulomb coefficients correspond to equal spin values $\sigma = \sigma'$ and are given by

$$A_{k m n}^\text{direct} = \sum_{l=0,2,4} F^l C^l(2m; 2m', 2m'') \times$$

$$\times \left\{ \gamma_{s M} \gamma_{s M} \delta_{s M} \lambda_{M} \lambda_{M} C^l \left(3, M_1 + \frac{1}{2}, 3, M_3 + \frac{1}{2} \right) + \gamma_{s M} \delta_{s M} \lambda_{M} \lambda_{M} C^l \left(3, M_1 + \frac{1}{2}, 3, M_4 + \frac{1}{2} \right) + \gamma_{s M} \delta_{s M} \lambda_{M} \lambda_{M} C^l \left(3, M_2 + \frac{1}{2}, 3, M_3 + \frac{1}{2} \right) + \gamma_{s M} \delta_{s M} \lambda_{M} \lambda_{M} C^l \left(3, M_2 + \frac{1}{2}, 3, M_4 + \frac{1}{2} \right) + \gamma_{s M} \delta_{s M} \mu_{M} \mu_{M} C^l \left(3, M_1 - \frac{1}{2}, 3, M_4 - \frac{1}{2} \right) + \gamma_{s M} \delta_{s M} \mu_{M} \mu_{M} C^l \left(3, M_2 - \frac{1}{2}, 3, M_4 - \frac{1}{2} \right) + \delta_{s M} \delta_{s M} \lambda_{M} \lambda_{M} C^l \left(3, M_1 - \frac{1}{2}, 3, M_3 - \frac{1}{2} \right) + \delta_{s M} \delta_{s M} \lambda_{M} \lambda_{M} C^l \left(3, M_2 - \frac{1}{2}, 3, M_3 - \frac{1}{2} \right) + \delta_{s M} \delta_{s M} \mu_{M} \mu_{M} C^l \left(3, M_2 - \frac{1}{2}, 3, M_4 - \frac{1}{2} \right) \right\}. $$

We have to compute the coefficients given by (16), $\alpha$ being one of the the two states of $\Gamma_7$ (called here $\Gamma_7^\alpha$). First, we found that the $l = 0$ component to all the $A_{k m n}^\text{direct} \lambda_{s M} \lambda_{M}$ (with $\beta = \Gamma_7^\beta$ or any state of $\Gamma_8$) is always zero. Then, the coefficient $A_{k m n}^\text{direct} \lambda_{s M} \lambda_{M}$ within the $\Gamma_7$ ground state is strictly equal to zero. Thus, the only non-zero terms correspond to $l = 2$ and $l = 4$ components of the direct Coulomb coefficients $A_{k m n}^\text{direct}$ from $\Gamma_7^\beta$.
to any state \( \Gamma'_s \) of the \( \Gamma_s \) quartet; it results that consideration of direct Coulomb interaction must increase the value of \( \beta \) defined in (1).

The calculation of \( 1/T_1 \) is straightforward but rather tedious. According to (6), there are three terms in \( 1/T_1 \): the first one comes from (7), the second one corresponds to the square of the direct Coulomb interaction constant, and the third term corresponds to the double product. The second term contains terms in \( (F^2)^2 \), \( (F^4)^2 \) and \( F^2 F^4 \); we can notice that the term in \( F^3 F^4 \) is almost negligible. The third term contains terms in \( F^2 G^1 \) and \( F^4 G^1 \), which are in fact much smaller than the terms in \( (F^3)^2 \) or in \( (F^4)^2 \).

Finally, the relaxation rate of the \( \Gamma_7 \) ground state is equal to:

\[
\frac{1}{T_1} = \frac{4\pi}{\hbar(2t+1)} \left[ \frac{3}{7} \frac{n(E_F)^4 G^1}{G^1} \right]^2 k_B T \left[ 1 + \beta \frac{\Delta/k_B T}{e^{\Delta/k_B T} - 1} \right]
\]

and the « acceleration coefficient » \( \beta \) is given by:

\[
\beta = 2 + 0.78 \left( \frac{F^2}{G^1} \right)^2 + 0.51 \left( \frac{F^4}{G^1} \right)^2 - 0.0085 \frac{F^2 F^4}{(G^1)^2} + 0.16 \frac{F^2}{G^1} + 0.043 \frac{F^4}{G^1}.
\]

In the present calculation yielding to the final expression (17), we have not described the enhancement of palladium host, because it is not obvious to introduce it phenomenologically as we have done in reference [1]. However, as we will see later on, such an effect could be phenomenologically taken into account in expression (17) by including it in the density of states \( n(E_F) \).

In order to improve the agreement with the experimental law (1) with respect to reference [1], we have theoretically computed both \( C_K \) and \( \beta \). If we fit the experimental value \( C_K = 120 \pm 20 \text{ MHz/K} \) by the expression (17), we immediately obtain:

\[
| n(E_F) G^1 | = 0.045.
\]

Such a small value for \( | n(E_F) G^1 | \) is quite typical of non-magnetic rare-earth impurities diluted in a non-magnetic matrix and is of the same order of magnitude as the value deduced for example by EPR studies for rare-earth impurities in palladium [9] or by superconductivity studies for LaGd alloys [10]. However, it is difficult to derive both \( n(E_F) \) and \( G^1 \) in the absence of any other information. There are clearly two extreme limiting cases: if we take the atomic value \( G^1 = 10 010.8 \text{ cm}^{-1} \) given by Chow [4], we obtain a density of states \( n(E_F) = 0.035 \text{ states/eV at.} \) which is clearly too small. On the other hand, if we take the value \( n(E_F) = 1.5 \text{ states/eV at.} \) for the total density of states of palladium given by Dye et al. [11], we obtain a value for \( G^1 = 0.03 \text{ eV} \), which is really much smaller than the atomic value \( G^1 = 1.25 \text{ eV} \). In fact, we cannot really deduce the values of \( n(E_F) \) and \( G^1 \) from equation (19) alone. We can however think that the case of PdYb alloys lies certainly between these two extreme limiting cases for the two following reasons: on one side, the exchange integral \( G^1 \) is greatly reduced by correlations in a metallic case compared to its atomic value. On the other side, the density of states \( n(E_F) \) entering expression (17) is smaller than the total density of states of palladium, because it corresponds to partial d-like wave functions; in the similar calculation of Fert et al. [8], the density of states which enters the expression for the relaxation rate is multiplied by a factor \( \sin^2 \delta_2 \), where \( \delta_2 \) is the phase shift of the d-virtual bound state, and it results that the effective density of states is reduced by a factor 1/10 in the case of PdYb alloys [8]. In conclusion, we cannot really evaluate \( n(E_F) \) and \( G^1 \), but the value given by (19) is reasonable for a normal rare-earth impurity.

But, the real improvement compared to the calculation of reference [1] concerns the «acceleration coefficient » \( \beta \). The main contribution to \( \beta \) comes from the three first terms of (18). For a qualitative point of view, there is clearly an improvement since \( \beta \) increases from 2 and is closer to the experimental value when the direct Coulomb integrals \( F^2 \) and \( F^4 \) are considered. But, it is rather difficult to have a quantitative agreement since we cannot have a precise determination of \( G^1, F^2 \) and \( F^4 \) in metallic PdYb alloys. However, if we take the extreme limiting case of atomic values for the exchange and Coulomb integrals, i.e. \( G^1 = 10 010.8 \text{ cm}^{-1} \) and \( F^4 = 11 415.5 \text{ cm}^{-1} \) given by Chow [4] and \( F^2 = 12 600 \text{ cm}^{-1} \) given by Fert and Levy [7], we obtain from (18) a theoretical value \( \beta = 4.14 \), in really excellent agreement with the experimental value \( \beta = 4.2 \pm 1.0 \).

Finally, we can make the two following comments: first, we have computed \( \beta \) by taking into account only the \( G^1 \) integral but in fact a full calculation including \( G^1, G^3 \) and \( G^5 \) would not have much modified the result. Second, we have only considered the d-f interaction which is certainly by far the most important and the most efficient to yield to a large value of \( \beta \); the consideration of the s-f interaction in addition to the d-f interaction would have introduced an extra parameter, without really modifying the final result.

3. Concluding remarks.

Thus we have shown the importance of the direct Coulomb d-f interaction for increasing the «acceleration coefficient » \( \beta \), since it acts only on transition probabilities from \( \Gamma_7 \) to \( \Gamma_8 \) and not on those within the ground state \( \Gamma_7 \). The importance of direct Coulomb integrals in the relaxation of ytterbium in palladium has also been shown by a parallel calculation [8] using the model Hamiltonian introduced by Lacueva et al. [6]. Such a model Hamiltonian is not so general
as our Hamiltonian (3) based on the formalism introduced in reference [3].
We have, therefore, found a better agreement with experiment for the acceleration coefficient $\beta$ than that previously obtained in reference [1], while a reasonable value is deduced for the product $|n(E_F)G^1|$. We have, moreover, obtained an excellent agreement with experiment for $\beta$ when we take the ratios of exchange and Coulomb integrals equal to their atomic values; however, there is no precise determination of these integrals in the real metallic case of PdYb alloys. Further experiments are clearly necessary to determine the importance and magnitude of the different d-f interaction terms in PdYb alloys.

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References