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Relaxation of ytterbium in palladium

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Résumé. — Nous montrons que l'on peut expliquer de façon satisfaisante la dépendance en température de la relaxation de Yb^{3+} dans le palladium en tenant compte de la partie non sphérique de l'interaction Coulombienne directe entre électrons 4f et électrons de conduction de caractère d.

Abstract. — We show that a satisfactory fit to the temperature dependence of the relaxation rate of ytterbium in palladium can be obtained by including the aspherical part of the direct Coulomb interaction between 4f electrons and the d part of the conduction electrons.

The paramagnetic relaxation rate of ytterbium in palladium was recently measured by Mössbauer experiments between 0.11 K and 2 K [1]. The data was fit to a Hirst-Orbach law [2] of the form :

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

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

C_K represents the coefficient of the Korringa relaxation taking place within the Γ_7 ground state and the acceleration coefficient β represents the presence of relaxation to an excited state at an energy Δ above the ground state. To fit the rapid rise of the relaxation above the Korringa rate one found that $\beta \sim 4$ was necessary, with $\Delta = 2.5$ K for the distance to the Γ_8 quadruplet and $C_K = (120 \pm 20)$ MHz/K. Usually ytterbium in metals is anomalous because the 4f electrons mix with the conduction electrons and the main contribution to the exchange interaction comes from the s-f mixing. However, ytterbium in palladium is normal ; the s-f mixing is not important and the Coulomb interaction provides the principal contribution to the exchange coupling. If one considers the conventional exchange interaction $-J_s.S$ one finds $\beta = 1$. By considering the *complete exchange* interaction between 4f electrons and conduction electrons with d character one was able to improve this coefficient to $\beta \sim 2$ [1].

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The *direct* Coulomb interaction between 4f and conduction electrons has been found to be very important in explaining the EPR and transport properties of noble metal with rare-earth impurities [3]. We will show that a satisfactory fit to the relaxation rates of ytterbium in palladium can be obtained by including the aspherical part of the direct Coulomb interaction between the 4f electrons and the d part of the conduction electrons. This interaction contributes to the relaxation by inducing transitions primarily to the excited states; therefore it immediately increases the acceleration coefficient β . First we consider the 4f-5d direct *and* exchange contributions to the relaxation; then at the end we incorporate the contribution from the 4f-6s exchange term.

The relaxation rate for Yb^{3+} in Pd is given as :

$$\frac{1}{T_1} = 2 W_{\Gamma_7 \rightarrow \Gamma_7} + \sum_{j=6,8} W_{\Gamma_7 \rightarrow \Gamma_j} \quad (2)$$

where $W_{\Gamma_7 \rightarrow \Gamma_7}$ is the transition probability within the ground state doublet and $W_{\Gamma_7 \rightarrow \Gamma_j}$ the probability of going from the ground to an excited crystal field state of Yb^{3+} , i.e. either Γ_8 or Γ_6 . As the Γ_6 doublet presumably lies far above the other states [1], Γ_7 and Γ_8 , and as the temperature is quite low, $T < 2$ K, we can easily neglect the transitions to Γ_6 and consider only excitations to the low lying excited quartet Γ_8 .

The transitions within the states of the Γ_7 doublet and between Γ_7 and Γ_8 are induced by the Coulomb interaction of the 4f electrons with the conduction electrons, i.e., by the k-f Coulomb interaction [4]. The transition probability between two states of Yb^{3+} (α and β) has been previously derived by us and is given as [3] :

$$W_{\alpha \rightarrow \beta} = \frac{k_B T f(\Delta_{\alpha\beta}/k_B T)}{8 \pi \hbar} N^2(E_F) \sum_{\sigma\sigma'} \int_{\Omega_k} \int_{\Omega_{k'}} |dT_{\alpha k \sigma \rightarrow \beta k' \sigma'}|^2 d\Omega_k d\Omega_{k'} \quad (3)$$

where dT represents the first order correction to the T matrix elements due to the k-f Coulomb interaction (direct and exchange) [3], $f(\Delta/k_B T)$ is given in equation (1), $\Delta_{\alpha\beta}$ is the energy separation between levels α and β , and $N(E_F)$ is the density of states of the conduction electrons at the Fermi level per unit volume for one spin direction. The correction to the T matrix is evaluated between states of the conduction electrons which take into account the *admixture* of ytterbium's 5d states. This admixture gives the main contribution to the Coulomb scattering. By using Friedel's theory of non-magnetic virtual bound states (VBS) the matrix element is written as [4] :

$$dT_{\alpha k \sigma \rightarrow \beta k' \sigma'} = \frac{4 e^{2i\eta_2} \sin^2 \eta_2}{\Delta_d N(E_F)} \sum_{mm'} \langle m' \sigma' | v_{\alpha\beta}(\mathbf{J}) | m \sigma \rangle Y_{2m}^*(\Omega_k) Y_{2m'}(\Omega_{k'}) \quad (4)$$

where $v_{\alpha\beta}$ is the matrix element of the perturbation between the states α and β of ytterbium, the sums on m and m' go over all five states of the 5d level, Δ_d is the half-width of the VBS and the phase shift η_2 is given as :

$$\eta_2 = \frac{\pi}{10} Z_d \quad (5)$$

where Z_d is the number of 5d electrons. The matrix elements in equation (4) can be written in terms of the elements of the 4f-5d Coulomb interaction. The general expression has been previously given by us [3] for $\text{Yb}^{3+}(4f^{13})$; the leading terms are given as :

$$\begin{aligned} v(J) = & -\frac{1}{7} (A_0 s + 6 A_1 l - 15\sqrt{7} A_2 (s^1 \times u^2)_d^1) \cdot \mathbf{J} - \\ & - (0.356 A_3 u_d^2 - 0.208 A_4 (s^1 \times u^1)_d^2 + 0.075 A_5 (s^1 \times u^3)_d^2) \cdot \Theta^2(J) + \dots \quad (6) \end{aligned}$$

where the dots represent higher-rank interactions. These higher rank terms have not been taken into account in previous analyses, and will not be considered in our analysis. The irreducible tensors u_d^k have unit reduced matrix elements (see Ref. [3]). The coefficients A_k are related to the Slater direct and exchange integrals and are given in tables V and VIII of reference [3].

By placing the perturbation $v(J)$ (Eq. (6)) in the expression for the transition probability (Eqs. (3) and (4)) and by performing the angular integrations over \mathbf{k} and \mathbf{k}' and the intermediate spin states σ' , we find :

$$W_{\alpha \rightarrow \beta} = 4 \sin^2 \eta_2 \frac{k_B T}{h \Delta_d^2} f(\Delta_{\alpha\beta}/k_B T) \text{Tr} (v_{\alpha\beta}^* v_{\alpha\beta}) \quad (7)$$

where we used $h = 2 \pi \hbar$ and the trace represents a sum over all ten 5d states, i.e.,

$$\text{Tr} (v_{\alpha\beta}^* v_{\alpha\beta}) \equiv \sum_{m=-2}^2 \sum_{\sigma} \langle m\sigma | v_{\alpha\beta}^* v_{\alpha\beta} | m\sigma \rangle .$$

Only spherical invariants of the 5d operators have a non-zero trace and contribute. These traces over the products of the angular momentum and irreducible tensor operators u^k of the 5d electrons entering equation (7) have been evaluated by repeatedly using the relation for recoupling four angular momenta [5] :

$$(a^{k_1} \times b^{k_2})^k \cdot (a^{k_1} \times b^{k_2})^k = \frac{2k+1}{(2k_1+1)(2k_2+1)} a^{k_1} \cdot a^{k_1} b^{k_2} \cdot b^{k_2} + \dots \quad (8)$$

where the terms on the right hand side which are traceless, i.e. non-scalar, have not been enumerated. To arrive at this relation we used the definition of the scalar product of two tensor operators :

$$a^k \cdot b^k = \sum_m (-)^m a_m^k b_{-m}^k$$

which is related to the irreducible tensor product of rank zero by :

$$a^k \cdot b^k \equiv \sqrt{2k+1} (a^k \times b^k)^0$$

By evaluating the traces entering equation (7) we find :

$$W_{\alpha \rightarrow \beta} = 4 \sin^4 \eta_2 \frac{k_B T}{h \Delta_d^2} \left\{ \frac{1}{49} \left(\frac{5}{2} A_0^2 + 720 A_1^2 + \frac{315}{2} A_2^2 \right) \langle \mathbf{J} \cdot W_{\alpha\beta} \mathbf{J} \rangle + \right. \\ \left. + \left[\frac{2}{5} (0.127) A_3^2 + \frac{5}{18} (0.043) A_4^2 + \frac{5}{98} (0.0056) A_5^2 \right] \langle \Theta^2 \cdot W_{\alpha\beta} \Theta^2 \rangle \right\} \quad (9)$$

where :

$$\langle \mathbf{J} \cdot W_{\alpha\beta} \mathbf{J} \rangle = \langle \alpha | \mathbf{J} | \beta \rangle \langle \beta | \mathbf{J} | \alpha \rangle f(\Delta_{\alpha\beta}/k_B T),$$

and similarly for the operator $\Theta^2(J)$.

The matrix elements of the 4f operators \mathbf{J} and $\Theta^2(J)$ have been evaluated for the Γ_7 and Γ_8 states of Yb^{3+} . Within the Γ_7 manifold ($f(\Delta/k_B T) = 1$) we find :

$$\langle \mathbf{J} \cdot W_{\gamma-\gamma} \mathbf{J} \rangle = 1/2(g/g_J)^2 = 9/2 \quad (10)$$

and

$$\langle \Theta^2 \cdot W_{\gamma-\gamma} \Theta^2 \rangle = 0 .$$

For transitions between Γ_7 and Γ_8 we find :

$$\langle \mathbf{J} \cdot \mathbf{W}_{7-8} \mathbf{J} \rangle = 9 f(\Delta/k_B T) \quad (11)$$

and

$$\langle \Theta^2 \cdot \mathbf{W}_{7-8} \Theta^2 \rangle = 105 f(\Delta/k_B T).$$

By placing these expectation values in the transition probability (Eq. (9)) and evaluating equation (2) we find the relaxation rate for Yb^{3+} in Pd can be written in the form of equation (1), where the Korringa relaxation coefficient is given by :

$$C_K = \frac{90}{49} (A_0^2 + 288 A_1^2 + 63 A_2^2) \frac{\sin^4 \eta_2}{\Delta_d^2} \frac{k_B}{h} \quad (12a)$$

and the acceleration coefficient is :

$$\beta = 1 + \frac{686}{3} \frac{[2/5(0.127) A_3^2 + 5/18(0.043) A_4^2 + 5/98(0.0056) A_5^2]}{[A_0^2 + 288 A_1^2 + 63 A_2^2]}. \quad (12b)$$

When we use the atomic values for the Coulomb integrals entering A_k (see Ref. [3]), $\Delta_d = 1$ eV for the half-width of the 5d VBS and $\eta_2 = \pi/10$, i.e., one 5d electron for ytterbium in palladium we find :

$$C_K = 24 \text{ MHz/K} \quad \text{and} \quad \beta = 10.8. \quad (13)$$

If the 5d state of ytterbium is split due to the cubic crystalline field of the surrounding matrix so that only the t_{2g} triplet state is occupied we must replace the trace in equation (7) by a double sum over the states of the triplet :

$$\sum_{\substack{\tilde{m}, \tilde{m}' \\ \sigma, \sigma'}} \langle \tilde{m} \sigma | v_{\alpha\beta}^* | \tilde{m}' \sigma' \rangle \langle \tilde{m}' \sigma' | v_{\alpha\beta} | \tilde{m} \sigma \rangle. \quad (14)$$

The transition probability when only the 5d- T_{2g} state is occupied has been evaluated previously by us [6] and we can readily write down the equivalent expressions to equation (12) for C_K and β . They are :

$$C_K = \frac{54}{49} \left(A_0^2 + \frac{288}{3} A_1^2 + \frac{135}{3} A_2^2 \right) \frac{\sin^4 \eta_t}{\Delta_t^2} \frac{k_B}{h} \quad (15)$$

and

$$\beta = 1 + \frac{686}{300} \frac{[9/2(0.81) A_3^2 + 0.24 A_4^2 + 0.03 A_5^2 - 0.09 A_4 A_5]}{\left[A_0^2 + \frac{288}{3} A_1^2 + \frac{135}{3} A_2^2 \right]}$$

where $\eta_t = \frac{\pi}{6} Z_d$. We have evaluated these expressions by using atomic values for the coefficients A_k [3], $\Delta_t = 1$ eV for the half-width of the 5d- t_{2g} VBS and $\eta_t = \frac{\pi}{6}$, i.e., one 5d electron for ytterbium in palladium, and we find :

$$C_K = 81 \text{ MHz/K} \quad (16a)$$

and

$$\beta = 9.2. \quad (16b)$$

We see that both solutions predict large values of β . This is because the aspherical Coulomb scattering gives rise to relaxation only by transitions to excited states and thus contributes to the Hirst-Orbach term and does not to the Korringa one. These values of β are independent of the phase shifts, η_2 or η_1 , and on the VBS width, Δ_d or Δ_i . They depend on the relative values of the Coulomb integrals A_2 and as mentioned, above, have been calculated by using atomic values of the A_k . A reduction of the A_k is expected in metals. However it cannot affect significantly β because the reduction factor seems to be approximately the same for all the A_k [3].

To go further we have now to take into account the contributions coming from other channels than $l = 2$, in particular the contribution coming from the $l = 0$ channel. This later contribution is expected to lower β . Therefore, we include the additional exchange between the 4f electrons and the s part of the conduction electrons of the form :

$$H_s = J_{fs} N^{-1} \mathbf{s} \cdot \mathbf{S} \delta(\mathbf{r}). \quad (17)$$

There is no interference between the relaxation in the $l = 0$ and $l = 2$ channels so that H_s provides an independent contribution to the relaxation, that is :

$$\frac{1}{T_1} = \frac{1}{T_1} \Big|_s + \frac{1}{T_1} \Big|_d. \quad (18)$$

The additional relaxation due to the s character of the conduction electrons has been previously evaluated [1], and is given as :

$$\frac{1}{T_1} \Big|_s = C_K^s T [1 + f(\Delta/k_B T)] \quad (19)$$

where :

$$C_K^s = 2 \pi^2 \left[\frac{g}{g_J} (g_J - 1) \right]^2 [J_{fs} N(E_F)]^2 \frac{k_B}{h}.$$

Note that the acceleration coefficient for this conventional exchange interaction is $\beta^s = 1$. By taking a value of $J_{fs} = 0.02$ eV [7], and $N(E_F) = 1.5$ eV⁻¹ atom⁻¹ [8], and the appropriate value of $g/g_J = 3$ and $g_J = 8/7$ for the ground doublet Γ_7 of Yb³⁺ ($J = 7/2$) we find :

$$C_K^s = 68 \text{ MHz/K}. \quad (20)$$

We now combine the s electron contribution to the relaxation coming from the t_{2g} VBS (Eq. (16)). We choose the t_{2g} solution because (1) the T_{2g} state is known to be primarily occupied for rare-earth in noble metals and (2) the final agreement is better with a t_{2g} VBS than with a 5d VBS. By combining equations (16), (19) and (20) we find that the relaxation rate for Yb³⁺ in Pd (Eq. (18)) is given as :

$$\frac{1}{T_1} = (68 + 80 \varepsilon) T \left[1 + \frac{68 + 9.2 \times 80 \varepsilon}{68 + 80 \varepsilon} f(\Delta/k_B T) \right] \quad (21)$$

where the parameter ε has been introduced to account for the reduction of the *atomic* 4f-5d Coulomb integrals to their *effective* values in metals [3]. This reduction is not necessary for the s electron contribution, as J_{fs} is already the *effective* coupling constant. From equation (21) we see that :

$$C_K = 68 + 80 \varepsilon \text{ MHz/K}$$

and

$$\beta = \frac{68 + 9.2 \times 80 \varepsilon}{68 + 80 \varepsilon}. \quad (22)$$

With $\varepsilon = 0.55$ we obtain $\beta = 4.22$; $C_K = 112$ MHz/K, to be compared with the experimental values, $\beta = 4.2 \pm 1$ and $C_K = 120$ MHz/K. The results on β and C_K have to be discussed separately. In our model β depends only on the weighting of the $l = 0$ and $l = 2$ channels, i.e. on the ratio of the parameters J_{fs} and ε . We have taken the value of J_{fs} estimated by Devine *et al.* [7] and a good agreement is then obtained with $\varepsilon = 0.55$, i.e. with a reduction of the Coulomb integrals by a factor $\sqrt{\varepsilon} = 0.74$. This value is close to what can be expected (for rare-earths in gold and silver the reduction factor of the Coulomb integrals has been estimated to be about 0.5). It thus appears that a good agreement is obtained for the acceleration factor β by a very plausible combination of the contributions from the $l = 2$ ($\beta = 9.2$) and $l = 0$ ($\beta = 1$) channels. The good agreement obtained for C_K is less significant because C_K depends on poorly known additional parameters, the number Z_t of d electrons ($Z_t = 10 \eta_d/\pi$) and the t_{2g} VBS width. We can only note that this agreement is obtained with reasonable values of these parameters. In our second solution with a 5d VBS a similar agreement could be obtained only by taking too small values of A_d .

In summary by assuming that the relaxation of ytterbium in palladium by the conduction electrons takes place through the 4f-5d and 4f-6s Coulomb interactions we are able to fit the data on the relaxation rate at low temperatures. The 4f-5d interaction has the quadrupolar term which couples the ground doublet Γ_7 to the excited states Γ_8 without creating any relaxation within the doublet. Therefore we find the appropriate acceleration coefficient β which describes the rapid rise of the relaxation above the Korringa rate given by $C_K T$. This large β was missing in the previous analyses of reference [1]. However we know that a new calculation taking into account the aspherical Coulomb scattering in the formalism of [1] is now in progress [9].

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