Influence of the crystalline field and Kondo effects on the relaxation rate: Application to Mössbauer experiments of ytterbium diluted in gold*

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Mössbauer experiments show that the relaxation rate of the doublet ground state Γ_7 in AuYb alloys, divided by the temperature, behaves logarithmically at low temperatures and rises very quickly above 10 K. This behavior is accounted for by computing the relaxation rate up to third order in the exchange integrals, with a Hamiltonian which decribes the resonant scattering of ytterbium impurities and takes into account both spin and orbit exchange scattering and crystalline field effect.

I. INTRODUCTION

It is well known that cerium, either in alloys such as LaCe, and YCe or in compounds such as $CeAl_2$ and $CeAl_3$, is magnetic and presents a Kondo effect due to the large resonant scattering which arises from the mixing between conduction and $4f$ electrons, because the cerium $4f$ level is close to the Fermi level. Such cerium alloys and compounds exhibit also a crystalline-field effect which affects deeply the nature of the Kondo effect.[1] An effective Hamiltonian, which takes into account the resonant-scattering mechanism and describes both the combined spin and orbit exchange scattering and the crystalline-field effect, has been previously derived for the $4f^1$ (or $4f^{13}$) configuration of cerium (or ytterbium) by use of the Schrieffer-Wolff transformation.[1] The third-order perturbation-theory resistivity computed with this Hamiltonian has successfully explained the experimental resistivities of $CeAl_2$ and $CeAl_3$ and, in particular, the peaks in the magnetic resistivity which correspond roughly to the over-all crystalline-field splitting. The conduction-electron relaxation by cerium impurities has been also previously computed by use of the effective exchange Hamiltonian, in order to account for recent EPR measurements of Gd in $LaAl_2$ with cerium impurities.[2]

On the other hand, ytterbium as an impurity dissolved in gold shows a resistivity minimum at low temperatures.[3] Ytterbium impurity is presently the only rare-earth element other than cerium which can present a Kondo effect. Thus the purpose of the present paper is to study the Kondo effect of ytterbium impurities in gold and to compute the relaxation rate of the ground state Γ_7 of ytterbium

in gold by considering the influence of the crystalline field on the Kondo effect within the previously described effective Hamiltonian.[1]

The AuYb alloys were previously a controversial case. Ytterbium as an impurity dissolved in some mixed gold-silver hosts was found to show a resistivity minimum at low temperature, but no resistivity minimum due to ytterbium was initially found in AuYb.[4,5] But more recently, a clear, although weak, minimum was experimentally observed in the resistivity of AuYb alloys.[3,6] Moreover, it was previously shown that the relaxation rate of Γ_7 divided by temperature, obtained in Mössbauer experiments, behaves logarithmically (with negative slope) from 0.6 to 6 K and has a minimum at 10 K.[7] On the other hand, nuclear-orientation[8] or magnetization[9] measurements at very low temperatures (some hundredths of K) give a normal saturation of the magnetization under applied field, indicating either no Kondo effect or a Kondo effect with a temperature smaller than $\frac{1}{100}$ K.[8] Thus all these experiments can be now easily interpreted by saying that the AuYb alloys are a Kondo system with a Kondo temperature smaller than 10 mK.

Let us now discuss in detail the Mössbauer experiments in AuYb alloys. Ytterbium diluted in gold is trivalent with the configuration $4f^{13}$; the large spin-orbit coupling gives a ground multiplet $j = \frac{7}{2}$, well separated from the $j = \frac{5}{2}$ multiplet. Then, the $j = \frac{7}{2}$ multiplet is split by the cubic crystalline field into a Γ_7 doublet for the ground state and two excited levels Γ_8 and Γ_6.[6,10] Let us call Δ_1 and Δ_2 the energy distances between Γ_7 and, respectively, Γ_8 and Γ_6, as shown on Fig. 1. According to magnetic susceptibility measurements, Δ_1 is either [10]80 or [16]94 K, and Δ_2 is either [10]83 or [16]91 K; so, the

two levels Γ_6 and Γ_8 are very close to each other and will in fact be taken together when analyzing the relaxation-rate data.

The relaxation rate of Γ_7 has been obtained by interpreting the Mössbauer relaxation spectra of the ^{170}Yb isotope, in the temperature range from 0.6 to 20 K.[7] In this temperature range, only Γ_7 is significantly populated, so that the relaxation theory is not too difficult to be worked out, and only the relaxation rate of Γ_7 is defined.[11] If we call $W = \frac{1}{2}T_1$ the spin-flip relaxation rate of Γ_7, the quantity $W/2\pi T$ behaves logarithmically with a negative slope below 6 K; these experimental results were the first evidence for a Kondo deviation to the Korringa linear law.[7] However, there is a minimum of $W/2\pi T$ at 10 K and a rapid increase of this quantity above 10 K, as shown on Fig. 5.

The logarithmic behavior below 6 K has been already explained[7] by considering the classical s-f exchange Hamiltonian

$$H = -2J_{sf}(g_J - 1)\vec{j} \cdot \vec{s} , \qquad (1)$$

where $\vec{j}$ is the total angular momentum of the ytterbium impurity, $\vec{s}$ the spin of the conduction electron, and g_J the Landé factor. The behavior of $W/2\pi T$ below 6 K has been accounted for by a classical Kondo calculation up to third order in J_{sf} and by choosing a value for $J_{sf} = -0.55$ eV.

However, in order to explain the minimum of $W/2\pi T$ at 10 K and its rapid increase up to 26 K, it is clearly necessary to invoke relaxation processes including the excited crystalline-field levels. These relaxation processes are the well-known Orbach ones which could be driven either by phonons or by conduction electrons. In dilute alloys, the relaxation processes due to conduction electrons are the most important ones at low temperatures, and they have been computed by Hirst[12] or Davidov et al.,[13] within the classical s-f exchange Hamiltonian (1) up to only the second order in the exchange integral J_{sf}.

Davidov et al.[13] have computed the thermal broadening of EPR linewidth which corresponds to the relaxation rate $1/T_2$, but in an isotropic case such as that studied here the two relaxation rates $1/T_1$ and $1/T_2$ are equal. However, their calculation was done only up to second order in the exchange integral J_{sf} within the classical s-f exchange Hamiltonian (1).

Moreover, according to the recent EPR experiments of Davidov et al.[13] or Rettori et al.,[14] the influence of the excited crystalline-field levels, in the framework of the second-order calculation of the thermal broadening of the EPR linewidth, becomes important at a temperature corresponding roughly to the third of the crystalline-field splitting, while, in the present Mössbauer experiments, the deviation to the logarithmic behavior occurs at a
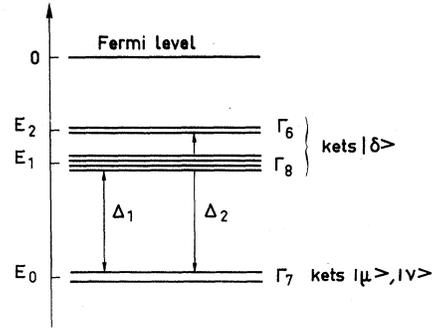
FIG. 1. Level scheme of Yb^{3+} in gold.

temperature corresponding roughly to $\frac{1}{15}$ of the crystalline-field splitting. Thus the calculation of Davidov et al.[13] cannot explain the behavior of $W/2\pi T$ in AuYb alloys, because it is a second-order calculation and cannot describe the logarithmic behavior below 6 K and also because the processes due to the excited levels appear to be too weak to account for the observed quick rise of $W/2\pi T$.

Thus we will compute here $W = 1/2T_1$ and we will improve the previous calculations[12,13] of the relaxation rate in the two following directions: First, we will consider the effective Hamiltonian of Ref. 1, which is more appropriate than the Hamiltonian (1) to describe the resonant scattering of Ytterbium, and then we will make the full treatment up to third order in the exchange integrals; these two improvements will allow us to describe both the Kondo effect and the crystalline field.

II. RELAXATION RATE OF A DOUBLET GROUND STATE

We compute in this section the spin-flip relaxation rate of a doublet ground state up to third order in the exchange integrals and within the framework of the effective Hamiltonian which takes into account the Kondo and crystalline-field effects.[1] This calculation will be applied to the Γ_7 ground state of AuYb alloys in Sec. III. We use here all the definitions and notations of Ref. 1. As in Ref. 1., we neglect here for ytterbium the normal Heisenberg-type exchange mechanism which leads to positive contributions to the exchange integrals and consider only the resonant-scattering mechanism, which is by far the most important one, because the exchange integrals needed to explain the behavior of $W/2\pi T$ are negative and of order $\frac{1}{2}$ eV in absolute value. Moreover, the case of the $4f^{13}$ configuration for ytterbium with one hole is exactly symmetric and can be treated exactly in the same way as the case of the $4f^1$ configuration for cerium with one electron.

In the case of ytterbium impurities in cubic symmetry, the eigenfunctions are given by

$$\Gamma_7 = \begin{cases} |j_z = +1.5\rangle = 0.8660 \left|+\tfrac{5}{2}\right\rangle - 0.500 \left|-\tfrac{3}{2}\right\rangle , \\ |j_z = -1.5\rangle = 0.8660 \left|-\tfrac{5}{2}\right\rangle - 0.500 \left|+\tfrac{3}{2}\right\rangle ; \end{cases}$$

$$\Gamma_6 = \begin{cases} |j_z = +1.17\rangle = 0.6455 \left|+\tfrac{7}{2}\right\rangle + 0.7638 \left|-\tfrac{1}{2}\right\rangle , \\ |j_z = -1.17\rangle = 0.6455 \left|-\tfrac{7}{2}\right\rangle + 0.7638 \left|+\tfrac{1}{2}\right\rangle ; \end{cases}$$

$$\Gamma_8 = \begin{cases} |j_z = +1.83\rangle = 0.7638 \left|+\tfrac{7}{2}\right\rangle - 0.6455 \left|-\tfrac{1}{2}\right\rangle , \\ |j_z = -1.83\rangle = 0.7638 \left|-\tfrac{7}{2}\right\rangle - 0.6455 \left|+\tfrac{1}{2}\right\rangle , \\ |j_z = +0.5\rangle = 0.500 \left|-\tfrac{5}{2}\right\rangle + 0.8660 \left|+\tfrac{3}{2}\right\rangle , \\ |j_z = -0.5\rangle = 0.500 \left|+\tfrac{5}{2}\right\rangle + 0.8660 \left|-\tfrac{3}{2}\right\rangle . \end{cases} \quad (2)$$

Let us call M the eigenvalue of one of these $4f$ eigenfunctions given by (2), $C_M^\dagger$ the creation operator for a $4f$ electron in the corresponding M substate, and $C_{kM}^\dagger$ the creation operator for a conduction-electron partial wavefunction of wave number k, total angular momentum $j = \tfrac{7}{2}$ with z-component $j_z = M$. So, the effective exchange Hamiltonian of Ref. 1 is given by

$$H = -\sum_{\substack{k,k' \\ M,M'}} J_{MM'} C_{k'M'}^\dagger C_{kM} (C_M^\dagger C_{M'} - \delta_{MM'} \langle n_M \rangle)$$

$$+ \sum_{\substack{kk' \\ M}} \mathcal{U}_{MM} C_{k'M}^\dagger C_{kM} . \quad (3)$$

In the Hamiltonian (3), the first term is only pure exchange scattering and the second term is only pure direct scattering which has no influence on the spin-flip relaxation rate. All the results concerning the Hamiltonian (3) are the same as those in the case of cerium. In particular, the exchange integrals $J_{MM'}$ are given by

$$J_{MM'} = \frac{|V_{kf}|^2}{2} \left(\frac{1}{E_M} + \frac{1}{E_{M'}} \right) .$$

V_{kf} is the mixing parameter between conduction and $4f$ electrons, $E_M (<0)$ designs here the energy of the crystalline-field level of M value compared to the Fermi level, and the scheme of levels for AuYb is given in Fig. 1.

An important feature of Hamiltonian (3) is that it allows matrix elements between all the crystal-field sublevels, with a weight given by $J_{MM'}$, and independent of the j or j_z values; so, the change in the magnetic quantum numbers $\Delta M = M' - M$ is no longer limited to ± 1 or 0 as for Hamiltonian (1). In particular, in the present case of ytterbium impurities in cubic symmetry, the eigenfunctions are given by (2), and with the Hamiltonian (1) the ground state of eigenvalue $M = +1.5$ has a zero matrix element with the state of eigenvalue $M = -1.17$ of Γ_6 or with the states $M = -1.83$ or $M = +0.5$ of Γ_8; moreover, the values of the matrix elements ob-

tained with (1) between the ground state $M = +1.5$ and the three other states $M = +1.17$, $M = 1.83$, and $M = -0.5$ are different from J_{sf}, because it enters in each matrix element j_z, j_+, and j_-. More precisely, the only two matrix elements connecting the ground state Γ_7 to the excited state Γ_6, i.e., the matrix elements $\langle M = 1.5 \, | j_+ | \, M = 1.17 \rangle$ and $\langle M = 1.17 | j_- | M = -1.5 \rangle$, are equal to zero and the Hamiltonian (1) connects the ground state Γ_7 only to the excited state Γ_8; finally, the only matrix elements which are not zero with (1) are $\langle M = 1.5 | j_- | M = 1.83 \rangle$, $\langle M = 1.5 | j_z | M = -0.5 \rangle$, $\langle M = 1.5 | j_+ | M = +0.5 \rangle$, $\langle M = -1.83 | j_z | M = -1.5 \rangle$, $\langle M = -0.5 | j_+ | M = -1.5 \rangle$, and $\langle M = 0.5 | j_z | M = -1.5 \rangle$. On the contrary, the Hamiltonian (3) connects the two levels of Γ_7 to all the levels of the excited states Γ_6 and Γ_8, and moreover, all the corresponding matrix elements with (3) are equal to $J_{MM'}$. Thus, if we consider the processes due to the crystalline field-excited levels, the Hamiltonian (3) has many more channels than the Hamiltonian (1) to relax the ytterbium impurity, and, if we look only at the first Born approximation, the effect of the excited levels will be much more efficient with the Hamiltonian (3) than with the Hamiltonian (1); we will see in the numerical example of Fig. 2 that the Hamiltonian (3) will be roughly seven times more
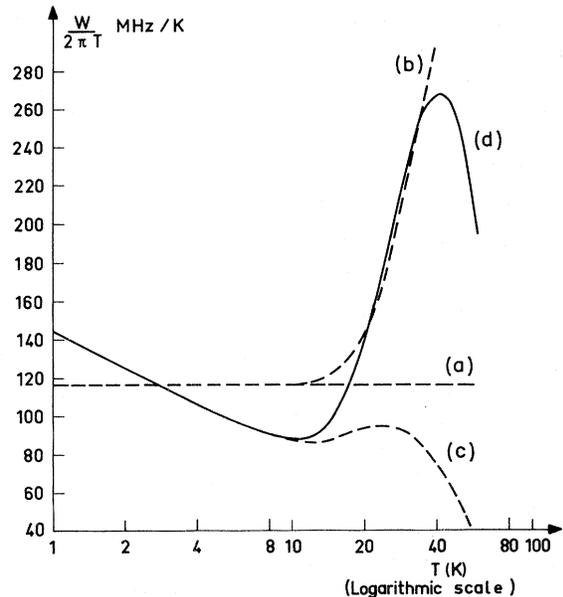
FIG. 2. Typical behavior of the relaxation rate divided by temperature vs log T. The values of the parameters are $\Delta = 100$ K, $E_0 = -200$ K, $V_{kf} = 0.08$ eV, $n(E_F) = 0.16$ (state) eV^{-1} (atom)$^{-1}$, and $D = 120$ K. The different contributions are (a) the Korringa law, i.e., second-order processes without crystal-field effects, (b) all second-order processes, (c) $W_{\mu\nu}/2\pi T$, second and third orders included, and (d) all processes, second and third orders included.

efficient than the Hamiltonian (1) at giving relaxation by the excited levels. If we add the effect of the third-order terms in $J_{MM'}$, it is easy to understand that the effect of the crystalline field will be visible at a much lower temperature with (3) than with (1). In fact, this point is certainly strong evidence, although indirect, for discriminating between the two Hamiltonians (1) and (3) in favor of the Hamiltonian (3). It is apparently the first crucial test which concludes that the Hamiltonian (3) is more appropriate than (1) for cerium and ytterbium because, as previously reported, there were really no such tests in the study of resistivities of cerium compounds.

For the calculation of the relaxation rate, let us call μ and ν the two states of the doublet ground state and δ all the excited states due to the crystal-field. The two states μ and ν are degenerate because the Mössbauer experiments have been done in zero field. Thus the relaxation rate of the doublet ground state can be written[12]

$$\frac{1}{T_1} = 2 W_{\mu\nu} + \sum_{\delta} W_{\mu\delta} , \qquad (4)$$

where $W_{\mu\nu}$ is the spin-flip scattering probability from the state μ to the state ν and $W_{\mu\delta}$ the scattering probability from the ground state μ to the excited state δ. In the second-order calculation, only the emptying rates of the ground state $W_{\mu\delta}$ are influenced by the presence of the excited levels, as previously shown by Hirst[12] or Davidov $et\ al.$[13] On the contrary, the excited levels give a contribution to both $W_{\mu\nu}$ and $W_{\mu\delta}$ in the third-order calculation.

The transition probabilities $W_{\alpha\beta}$ are given by

$$W_{\alpha\beta} = \frac{4\pi}{\hbar(2j+1)} \sum_{\substack{k,M \\ k',M'}} |T_{\alpha kM \to \beta k'M'}|^2 f_{kM}(1 - f_{k'M'})$$

$$\times \delta(\epsilon_{kM} + E_\alpha - \epsilon_{k'M'} - E_\beta) . \qquad (5)$$

$T_{\alpha kM \to \beta k'M'}$ is the scattering amplitude of the process in which the impurity goes from the state α to the state β while the conduction electron is going from the partial state kM to the partial state $k'M'$; the Fermi-Dirac functions f_{kM} and $f_{k'M'}$ are introduced as usual to give a filled-up initial state kM and an empty final state $k'M'$ for conduction electrons, and there is equality of the energy $\epsilon_{kM} + E_\alpha$ for the initial state and the energy $\epsilon_{k'M'} + E_\beta$ for the final state. Finally, the factor $1/(2j+1)$ measures the weight of the partial wave function $|kM\rangle$, and the factor $2/(2j+1)$ has been introduced in (5) to go from the representation of the states $|\vec{k}\sigma\rangle$ with plane waves of spin σ to the representation of the states $|kM\rangle$ with partial wave functions of wave number k, $j = \frac{7}{2}$ and $j_z = M$.

The scattering amplitude $T_{\alpha kM \to \beta k'M'}$ has been com-

puted in Ref. 1 with the Hamiltonian (3) and is given by the expression (33) of Ref. 1. (There is a misprint in formula (33) of Ref. 1, and one has to read the opposite sign for the last term corresponding to the second Born approximation; this error concerns only expression (33) and has not been transmitted to the following relations of Ref. 1.)

For $\alpha \neq \beta$, which is the only case of interest here, the scattering amplitude is written

$$T_{\alpha kM \to \beta k'M'} = -\delta_{\alpha M'}\delta_{\beta M}$$

$$\times \left(J_{MM'} + \sum_m J_{mM} J_{mM'} g(\epsilon_{k'} + E_m - E_M) \right) , \qquad (6)$$

where the sum over m is made over all the possible levels due to the crystalline field, and the function $g(\epsilon)$ is given as usual by

$$g(\epsilon) = \sum_q \frac{f(\epsilon_q)}{\epsilon_q - \epsilon} . \qquad (7)$$

The scattering amplitudes entering the two probabilities of W are given by

$$T_{\mu kM \to \nu k'M'} = -J_{\mu\mu} - \sum_m J_{m\mu}^2 g(\epsilon_{k'} + \Delta_m) , \qquad (8)$$

$$T_{\mu kM \to \delta k'M'} = -J_{\delta\mu} - \sum_m J_{m\delta} J_{m\mu} g(\epsilon_{k'} + \Delta_m) , \qquad (9)$$

where

$$\Delta_m = E_m - E_\mu . \qquad (10)$$

Before going further, let us give the form of the function $g(\epsilon)$ and of the different integrals which will enter the calculation. All the calculations are reported in the work of Beal-Monod and Weiner[16] or in Ref. 1. The function $g(\epsilon + \Delta)$ is given by

$$g(\epsilon + \Delta) = \sum_q \frac{f(\epsilon_q)}{\epsilon_q - \epsilon - \Delta}$$

$$= n(E_F)\left[2 + \ln\frac{kT}{2D} - I\left(\frac{\epsilon + \Delta}{kT}\right) \right] , \qquad (11)$$

where $n(E_F)$ is the density of states of the conduction band at the Fermi level for one spin direction, D is the cut-off of the interaction $J_{MM'}$ measured from the Fermi energy, and $I((\epsilon + \Delta)/kT)$ is

$$I\left(\frac{\epsilon + \Delta}{kT}\right) = \int \frac{\partial f(\epsilon')}{\partial \epsilon'} \ln\left|\frac{\epsilon' - \epsilon - \Delta}{2kT}\right| d\epsilon' . \qquad (12)$$

We perform the calculation of the relaxation rate by transforming the sum over k and k' in (5) into an integration over the energies. The calculation involves the integrals[16]

$$\int \frac{\partial f(\epsilon)}{\partial \epsilon} \frac{d\epsilon}{1 - f(\epsilon)(1 - e^{-\Delta/kT})} = -\frac{\Delta}{kT}\frac{e^{\Delta/kT}}{e^{\Delta/kT} - 1} , \qquad (13)$$

$$\int \frac{\partial f(\epsilon)}{\partial \epsilon} I\!\left(\frac{\epsilon+\Delta}{kT}\right) d\epsilon = I_1\!\left(\frac{\Delta}{kT}\right) , \qquad (14)$$

$$\int \frac{\partial f(\epsilon)}{\partial \epsilon} \frac{I((\epsilon+\Delta)/kT)}{1-f(\epsilon)(1-e^{-\Delta/kT})} d\epsilon$$

$$= \int \frac{\partial f(\epsilon)}{\partial \epsilon} \frac{I(\epsilon/kT)}{1-f(\epsilon)(1-e^{-\Delta/kT})} d\epsilon$$

$$= \frac{\Delta}{kT} \frac{e^{\Delta/kT}}{e^{\Delta/kT}-1} I_2\!\left(\frac{\Delta}{kT}\right) . \qquad (15)$$

The functions $I_1(x)$ and $I_2(x)$ have been computed numerically and shown graphically in Ref. 16. The asymptotic forms of these two functions for low temperatures, i.e., $kT < \frac{1}{10}\Delta$, are

$$I_1(\Delta/kT) \simeq \ln|\Delta/2kT| - 3.27(kT/\Delta)^2 + \cdots , \qquad (16a)$$

$$I_2(\Delta/kT) \simeq \ln|\Delta/2kT| - 1 + 3.27(kT/\Delta)^2 + \cdots . \qquad (16b)$$

At last, the two terms entering $1/T_1$ in expression (4) are easily computed. Let us denote the ground state by the index 0 and excited states by the index $i = 1, 2, \ldots, N$, with the respective degeneracies α_0 and α_i. So, we have

$$2W_{\mu\nu} = \frac{8\pi}{\hbar(2j+1)} [J_{00}n(E_F)]^2 kT$$

$$\times \left\{ 1 + 2\alpha_0 J_{00}n(E_F)\left(1.568 + \ln\frac{kT}{2D}\right) \right.$$

$$\left. + 2\sum_{i=1}^{N} \alpha_i \frac{J_{0i}^2}{J_{00}} n(E_F)\left[2 + \ln\frac{kT}{2D} + I_1\!\left(\frac{\Delta_i}{kT}\right)\right] \right\} , \qquad (17)$$

and

$$\sum_{\delta} W_{\mu\delta} = \frac{4\pi}{\hbar(2j+1)} \sum_{i=1}^{N} \frac{\alpha_i \Delta_i}{e^{\Delta_i/kT}-1} [J_{i0}n(E_F)]^2$$

$$\times \left\{ 1 + 2n(E_F)\left[2 + \ln\frac{kT}{2D} + I_2\!\left(\frac{\Delta_i}{kT}\right)\right] \right.$$

$$\left. \times \left(\alpha_0 J_{00} + \sum_{j=1}^{N} \alpha_j J_{jj}\right) \right\} , \qquad (18)$$

and $1/T_1$ is given by (4) with (17) and (18).

In the case of AuYb alloys, we take the simplified picture of two levels, the ground state Γ_7 with $\alpha_0 = 2$ and only one excited state with $\alpha_1 = 6$, for describing together Γ_6 and Γ_8; the distance between the two levels is called Δ. So, $1/T_1$ is given for AuYb alloys by

$$\frac{1}{T_1} = \frac{8\pi}{\hbar(2j+1)} [n(E_F)]^2 \left(J_{00}^2 kT + \frac{3J_{01}^2 \Delta}{e^{\Delta/kT}-1}\right)$$

$$+ \frac{8\pi}{\hbar(2j+1)} [n(E_F)]^3 \left\{ 4J_{00}^3 kT \left(1.568 + \ln\frac{kT}{2D}\right) \right.$$

$$+ 12 J_{00}J_{01}^2 kT \left[2 + \ln\frac{kT}{2D} + I_1\!\left(\frac{\Delta}{kT}\right)\right]$$

$$\left. + 6J_{01}^2(J_{00} + 3J_{11})\frac{\Delta}{e^{\Delta/kT}-1} \right.$$

$$\times \left[2 + \ln\frac{kT}{2D} + I_2\!\left(\frac{\Delta}{kT}\right)\right] \right\} . \qquad (19)$$

The results obtained with the formula (19) for AuYb alloys are discussed in the next paragraphs, but let us compare here the formula (19) to the similar formula obtained by Davidov et al.[13] for the Hamiltonian (1). The thermal broadening of the EPR linewidth, given by formula (3) of Ref. 13, can be written

$$\Delta H = \frac{9\pi}{g\mu_B}[(g_J - 1)n(E_F)J_{sf}]^2 \left(kT + \frac{\Delta}{e^{\Delta/kT}-1}\right) . \qquad (20)$$

Similarly, the relaxation rate obtained with (1) can also be written

$$\frac{1}{T_1} = \frac{4\pi}{\hbar}\left(g\frac{g_J-1}{g_J}n(E_F)J_{sf}\right)^2 \left(kT + \frac{\Delta}{e^{\Delta/kT}-1}\right) , \qquad (21)$$

where g is the effective g value for the Γ_7 ground state. So, the formula (21) obtained with the Hamiltonian (1) has to be compared with the two first terms of formula (19) obtained with the Hamiltonian (3). This is done in Sec. III.

III. THEORETICAL RESULTS FOR THE THERMAL DEPENDENCE OF THE RELAXATION RATE

We present here the main results of the model, and we will compare our theoretical results to the experiments in AuYb alloys only in Sec. III. We will discuss here the results concerning the quantity $W/2\pi T = 1/4\pi T_1 T$ rather than $1/T_1$, because the Kondo contributions will appear more clearly.

In the case of AuYb, we take $\Delta_1 = \Delta_2 = \Delta$ and the relaxation rate is given by (19); we choose also the density of states $n(E_F) = 0.16$ (states)/eV (atom) of pure gold and $V_{kf} = 0.08$ eV as in the case of cerium.[1,15] These three assumptions will be kept throughout the remainder of the paper and, in particular, will be used for the derivation of Figs. 2–5.

Figure 2 gives a typical behavior of $W/2\pi T$ versus $\log T$, in order to show its different contributions. The curve (a) corresponds to the first term of (19), which is proportional to J_{00}^2; it is in fact the Korringa relaxation of the ground state as it would be alone, i.e., only spin-flip terms of $W_{\mu\nu}/2\pi T$ in second order in exchange integral are taken into account, leading to a constant for W/T. This is the well-known behavior of the relaxation of a Kramers doublet isolated from the excited crystal-line-field levels and in the absence of Kondo effect. The curve (b) represents all second-order contributions, i.e., the two first terms of (19) which are proportional to

$$J_{00}^2 + 3J_{01}^2 \frac{(\Delta/kT)}{(e^{\Delta/kT}-1)} .$$

This is the behavior shown in (a) plus real Orbach-

Hirst-type processes computed up to the second order. The curve (b) corresponds exactly to the same limitation as the calculation of Davidov *et al.*[13] for the thermal broadening of the EPR linewidth computed with the Hamiltonian (1). The curve (c) gives the total spin-flip contribution $W_{\mu\nu}/2\pi T$, including both second-order or third-order terms, as given by the relation (17); it corresponds in the expression (19) to the first term in J_{00}^2 and to the third and fourth terms, respectively, in J_{00}^3 and $J_{00} J_{01}^2$. These third-order terms correspond to "virtual" processes giving spin flip in the ground state with a scattering inside the excited levels; the third-order term in J_{00}^3 gives the simple logarithmic Kondo behavior at low temperatures, while the third-order term in $J_{00} J_{01}^2$ gives an increasing deviation from the logarithmic law which starts initially in T^2 at low temperatures, according to (16a). At last, the curve (d) gives the total relaxation rate given by (19); the curve (d) is obtained from the curve (c) by adding the second term of (19) and the last one in J_{01}^2 ($J_{00} + 3J_{11}$). All these curves have been drawn numerically with the set of parameters $\Delta = 100$ K, $E_0 = -200$ K, $D = 120$ K. This set of parameters is very close to that used in Fig. 5 for fitting the best the experimental results for AuYb.

At this step of the calculation, it is interesting to compare our results to the second-order calculation of Davidov *et al.*[13] given by (20) and (21); in this case which has been applied to alloys such as AgDy or AuEr, the linewidth deviates from the Korringa law at a temperature of order $\frac{1}{3}\Delta$ or $\frac{1}{4}\Delta$. This point has to be compared to the second-order curve (b) of Fig. 2, which deviates from a constant between 10 and 15 K, i.e., between $\frac{1}{10}\Delta$ and $\frac{1}{6}\Delta$. The discrepancy can be explained as follows: in the two cases, the thermal dependence of the second-order contribution to $1/T_1$ is given by the function $F(T)$,

$$F(T) = kT \left(1 + A \frac{\Delta/kT}{e^{\Delta/kT} - 1}\right) . \tag{22}$$

The coefficient is equal to $A = 3(J_{01}/J_{00})^2$ in our model and is consequently equal to 6.75 in the numerical example of Fig. 2. On the contrary, A is equal to 1 within the *s-f* classical Hamiltonian (1); this result is conserved if there is only the Γ_8 as an excited state, as in AgDy or AuEr,[13] because the Hamiltonian (1) does not connect the states Γ_6 and Γ_7. Thus the present experiment can apparently discriminate between the two Hamiltonians in favor of the Hamiltonian (3). At last, we can suggest an experiment which will be very interesting, although it is presently academic, to discriminate between the two models: If there exists a system with the Γ_7 ground state and with the Γ_6 state as the first excited level, well separated from the Γ_8 state, there will be no effect of crystalline field

with the Hamiltonian (1) and there will be a strong effect with the Hamiltonian (3).

Thus the second-order terms arising from (19) deviate from the Korringa law at a temperature smaller than the second-order terms arising from (21); but this effect has the same origin in the two cases and originates from the population of the excited levels, and, in this sense, we can call these processes "real" ones. But the main effect of deviation on the final curve (d) arises from the third-order terms and this effect has a completely different origin; if we look at the curves (c) or (d) of Fig. 2, we see that these curves begin to depart from a logarithmic behavior at 5 or 6 K, i.e., between $\frac{1}{20}\Delta$ or $\frac{1}{15}\Delta$. At such temperatures, the excited levels are not really populated, and the influence of the excited levels arises because the electrons in the intermediate state of the Kondo scattering processes lie in these excited levels; in this sense, we can call these processes "virtual" ones. Thus the introduction of the third-order terms extends very much the temperature range in which the crystalline-field-excited levels have an influence on the relaxation rate.

We have seen that the expression (19) depends on three parameters if we take $n(E_F)$ and V_{kf} as fixed quantities. Moreover, the parameter D is a theoretical one and has no real importance here, because it gives essentially a vertical translation of the curves. So, we discuss here only the role of the two physical parameters E_0 and Δ, or, in other words, J_{00} and Δ/E_0. The parameter J_{00} gives the slope of the Kondo logarithmic behavior at low temperatures, while Δ/E_0 fixes the temperature of the minimum and the rapidity of the increase of $W/2\pi T$ after the minimum with respect to the low temperature decrease.

Figures 3 and 4 show, respectively, the influence of E_0 and of Δ; in the two figures we take $n(E_F)$ = 0.16 (states)/eV (atom), $V_{kf} = 0.08$ eV, $D = 120$ K. Figure 3 shows curves for three different values of E_0 around 200 K for $\Delta = 100$ K, and Fig. 4 shows curves for three different values of Δ around 100 K for $E_0 = -200$ K.

In Fig. 3 we see clearly that the absolute value of the negative slope of the logarithmic behavior at low temperatures and the rapidity at which $W/2\pi T$ increases after the minimum increase both when $|E_0|$ decreases or $|J_{00}|$ increases. In Fig. 4 we see that the slope of the logarithmic behavior at low temperatures does not change with Δ and that the influence of Δ is essentially to shift the curve parallel to the temperature axis; in particular, the minimum of the $W/2\pi T$ curve increases when Δ increases.

At last, all the curves go through a maximum at a temperature a little smaller than half the crystalline-field splitting. But, at such a temperature,
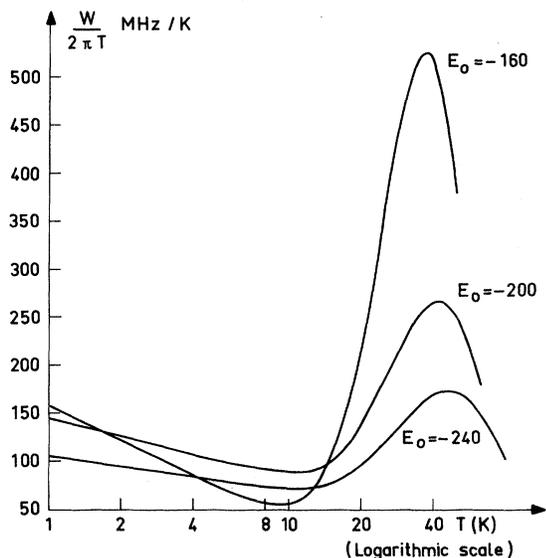
FIG. 3. Dependence of $W/2\pi T$ on E_0. The values of the fixed parameters are $\Delta = 100$ K, $V_{kf} = 0.08$ eV, $n(E_F) = 0.16$ (state) eV^{-1} (atom)$^{-1}$, and $D = 120$ K. The different E_0 values are indicated in K in the figure.

the excited levels become really populated and the analysis of the Mössbauer spectra in term of an unique Γ_7 relaxation rate is no longer valid at this temperature.

We have finally to note that the perturbation method used here is perfectly valid in the temperature range where we will apply the theory, i.e., from 0.6 K to less than 30 K. If we compare the curves (b) and (d), we immediately see that, in this temperature range, the ratio of the third-order term and of the second-order term is always less than 0.3. Thus the limitation of the range of temperature in which we can apply the present model does not come from the perturbation method, but rather from the analysis of the Mössbauer spectra used to obtain the relaxation rate of the ground state Γ_7.

IV. COMPARISON WITH EXPERIMENT IN AuYb ALLOYS

The experimental method used for studying the Mössbauer spectra of AuYb has been already described elsewhere.[7,11] We recall that the studied samples are Au^{170}Tm sources, obtained by irradiating by neutrons the thulium metal before melting it with gold. The active thulium is the ^{170}Tm isotope, which is the source to study the Mössbauer effect on ^{170}Yb. Figure 5 shows the experimental points for $W/2\pi T$, measured from 0.6 to 26 K; these data are obtained for a nominal concentration of 500 ppm of thulium in gold, which corresponds to ytterbium concentrations smaller than 1 ppm. In a preceeding paper,[7(b)] the low-temperature region

from 0.6 to 6 K was studied with special care; two samples of 500 and 2000 ppm of thulium were studied, and the relaxation rate was found to be independent of thulium concentration when the static broadening of the lines introduced by the concentration in the spectra was correctly taken into account. As shown in Fig. 5, new experiments have been performed to have a best precision in the temperature region above 6 K, giving roughly the same results as in a previous paper for another sample containing 2000 ppm of thulium.[7(a)] These improvements concerning thulium concentrations were important for checking the assumption that the relaxation was really due to isolated ytterbium impurities interacting only with conduction electrons and for ruling out completely a possible influence of thulium impurities, which present in gold a first excited magnetic state Γ_5 located at 7 K[10] above the nonmagnetic ground singlet Γ_2.

The relaxation theory and the fitting procedure which allow us to obtain the relaxation rate of the doublet ground state Γ_7 from the experimental spectra have been also explained elsewhere.[11,7] However, we should like to emphasize that, when fitting the Mössbauer relaxation spectra, the minimum experimental linewidth must be correctly evaluated. In the present case, where we study sources, the adopted value is 2.7 mm/sec, obtained with the same ^{170}YbB$_6$ single-line absorber and a TmB$_2$ source (knowing the Debye temperature of the absorber,[17] this corresponds practically to a natural width for the source, the broadening coming essentially from the effective width of the absorber). To check that in doing this we have a correct evaluation of the relaxation, experiments have been performed with the present Au^{170}Tm source at 70 K. The
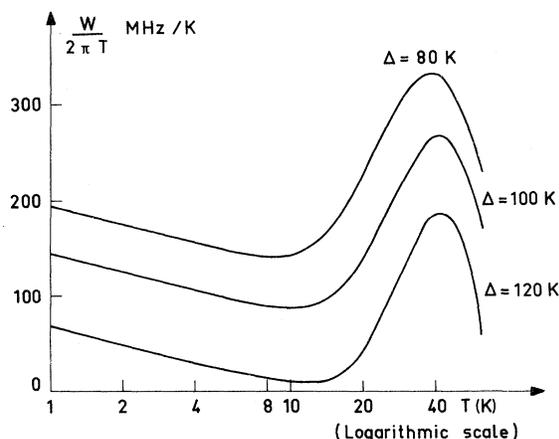
FIG. 4. Dependence of $W/2\pi T$ on Δ. The values of the fixed parameters are $E_0 = -200$ K, $V_{kf} = 0.08$ eV, $n(E_F) = 0.16$ (state) eV^{-1} (atom)$^{-1}$, and $D = 120$ K. The different Δ values are indicated in K in the figure.
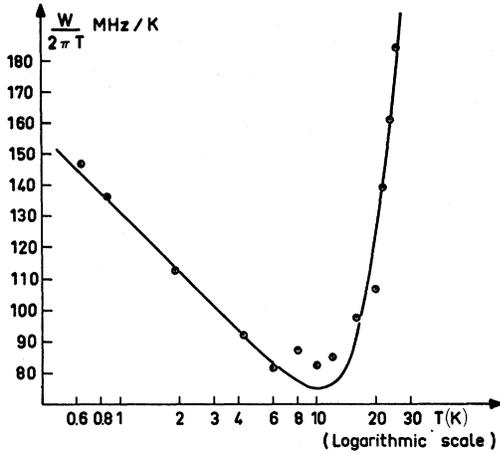
FIG. 5. Plot of $W/2\pi T$. The points are the experimental results for AuYb alloys and the full line is the theoretical fit, with the parameters $\Delta = 100$ K, $E_0 = -197.5$ K, $V_{kf} = 0.08$ eV, $n(E_F) = 0.16$ (state) eV^{-1} (atom)$^{-1}$, and $D = 113.7$ K.

linewidth of the single line obtained at this temperature is 3.1 mm/sec, i.e., only 15% larger than the minimum one assumed. For comparison, the spectrum at 26 K has approximately a width of 6.2 mm/sec.

Finally, it is necessary to clear up here two points concerning the applicability of the relaxation theory. First, when relaxation processes of the doublet ground state involve higher crystal-field levels, it would be rigorously necessary to treat the relaxation problem of the complete $j = \frac{7}{2}$ manifold. However, if the temperature is sufficiently low compared to the distance between the ground state and the excited states, so that the excited levels are not significantly populated, the observed relaxation spectrum corresponds to that of the ground level and the effect of the excited ones is summarized in an extra relaxation rate, for example here the second contribution of relation (4).[18] Consequently, we will apply the model developed here up to 26 K, which corresponds to $\frac{1}{3}\Delta$ or $\frac{1}{4}\Delta$, so that the applicability of the present model seems reasonable up to that temperature. The second point is that the used line-shape relaxation theory is the classical second-order (in exchange integrals) perturbation method. But, Hartmann-Boutron[19] has recently shown that, at temperatures where the "extreme-narrowing" condition is fulfilled, i.e., $kT \gg \hbar\omega_{hf}$, where $\hbar\omega_{hf} = 0.11$ K (Ref. 20) is the hyperfine separation, the complete line-shape relaxation treatment up to third order takes the form of the second-order one, but with a relaxation rate containing both second- and third-order contributions. So, we can identify the relaxation rates obtained experimentally by application of the classical

second-order treatment with the ones calculated in Sec. II of the present work.

According to these two considerations, we have limited here the temperature range where we compare experiment and theory to that shown on Fig. 5, i.e., from 0.6 to 26 K. Another reason to limit ourselves to temperatures not too high is that here only processes driven by conduction electrons have been considered and processes driven by phonons have been neglected.

The experimental data of Fig. 5 have been fitted by the formula (19) of the present model. We take the density of states $n(E_F) = 0.16$ (states)/eV (atom) equal to that of pure gold and the reasonable value $V_{kf} = 0.08$ eV. On the other hand, we choose the three other parameters Δ, E_0, and D in order to fit best the experimental data. The quick rise of $W/2\pi T$ above 10 K gives a value of Δ equal to 100 ± 10 K, in very good agreement with previous magnetic-susceptibility results.[6,10] The logarithmic slope of $W/2\pi T$ at low temperatures fixes the two remaining parameters, and the full line corresponds to the theoretical formula (19) with $\Delta = 100$ K, $E_0 = -197.5$ K, and $D = 113.7$ K. The deduced values for the exchange integrals are

$$J_{00} = -0.37, \quad J_{01} = -0.56, \quad J_{11} = -0.76 \text{ eV}. \quad (23)$$

Thus the value of J_{00} chosen here to fit the best the experimental data is slightly larger in absolute value than the corresponding values used for cerium in alloys such as LaCe.[1] The consequence is that, if we take the same V_{kf} value here as in the case of cerium alloys, we obtain a relatively small $|E_0|$ value of order 200 K and an again smaller $|E_1|$ value of order 100 K. But the Schrieffer-Wolff method used here, which treats V_{kf} as a small quantity, is still valid, because the Hartree-Fock half-width of the virtual bound state is smaller than $|E_0|$ and $|E_1|$ owing to the small value of $n(E_F)$.[1]

However, we can say that the parameters obtained to fit the data are reasonable and, in particular, that the value of the only parameter Δ which can be really checked by another experimental method is in very good agreement with the value found by this other experiment of magnetic susceptibility.[6,10]

We can estimate the Kondo temperature of the doublet ground state Γ_7 defined usually as the temperature at which the third-order term is twice the second-order term. We find that the theoretical Kondo temperature of AuYb alloys corresponding to the full curve of Fig. 5 is very low and, more precisely, much smaller than 1 mK. This estimate cannot obviously be checked, but it agrees reasonably with nuclear-orientation[8] or magnetization[9] experiments, which give an experimental Kondo temperature smaller than 10 mK.

Thus the present model, which describes the

resonant scattering of ytterbium by the Hamiltonian (3) and which treats both the Kondo and the crystalline-field effects, can explain fairly well the experimentally observed relaxation rate of AuYb alloys; in particular, the model accounts for the logarithmic behavior at low temperatures and for the departure from this law at a temperature of order $\frac{1}{15}$ of the distance between the doublet ground state and the excited states. These points are different from the results of the second-order Davidov et al.[13] calculation, which yields a departure from the Korringa law at a temperature of order $\frac{1}{3}$ the

distance between the ground and the excited levels. This discrepancy arises both from considering the "virtual" processes coming from Kondo-type scattering and from the Hamiltonian (3), which connects equally all the possible levels of the $j = \frac{7}{2}$ configuration, in strong contrast to the classical s-f exchange Hamiltonian.

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