PHYSICAL REVIEW B VOLUME 9, NUMBER 1 1 JANUARY 1974

Mössbauer effect in the presence of electronic relaxation: Application to the ^{170}Yb nucleus[*]

F. Gonzalez-Jimenez[†] and P. Imbert
Service de Physique du Solide et de Résonance Magnétique; Centre d'Etudes Nucléaires de Saclay, BP n° 2-91190 Gif-sur-Yvette, France

F. Hartmann-Boutron
Laboratoire de Physique des Solides,[‡] Université Paris Sud, 91405 Orsay, France

(Received 22 May 1973)

In this study of the Mössbauer line shape in the presence of electronic relaxation, we first compare the stochastic model of Clauser and Blume with the perturbation theory of Hirst and discuss the physical concepts underlying these two theories. We then derive the algebraic expression for the Mössbauer line shape in the presence of relaxation for a nuclear transition ($2^+ \rightarrow 0^+$) in the case of an electronic spin $S = 1/2$ and of axial hyperfine interactions; the resulting formulas were applied to a case of isotropic hyperfine interactions, i.e., to the relaxation spectra of ^{170}Yb in gold.

I. INTRODUCTION

Recently two theories have been advanced in order to compute the effects of electronic relaxation on the Mössbauer spectra: the stochastic theory of Clauser and Blume[1] and the perturbation treatment of Hirst.[2] We first recall the main lines of these two types of calculations. As regards *Hirst's theory*, we emphasize that it differs from conventional relaxation calculations in that the "secular approximation", which is neither necessary from a theoretical point of view nor compatible with experimental conditions, is not retained; we also discuss the conditions of validity of the perturbation treatment. Then assuming that relaxation is due to a fluctuating field acting on the electronic spin and that it has a "spherical" character ("extreme narrowing" and isotropic instantaneous fluctuations), we derive the form of the relaxation matrix and relate the spectral density of the fluctuating field to the longitudinal relaxation time T_1 of the electronic spin S. We then demonstrate that in the simple case worked out by them (pulses of form $\vec{h}\cdot\vec{S}$), *Clauser and Blume's theory* is formally equivalent to that of Hirst in two cases: any S when the stochastic pulses are small, and any amplitude of the pulses when $S = \frac{1}{2}$.

As an application, we consider the case of a Mössbauer transition ($2^+ \rightarrow 0^+$) (frequently encountered in rare-earth nuclei) for which we derive the form of the relaxation spectra in the presence of axial interactions and of an effective electronic spin $S = \frac{1}{2}$. Finally we describe and interpret the experimental results we have obtained[3] on ^{170}Yb diluted in gold, in a cubic substitutional position, where its hyperfine interaction inside the lowest electronic level Γ_7 (with effective spin $S = \frac{1}{2}$) is isotropic.

II. ATOMIC SYSTEM, ITS COUPLING WITH LATTICE, MÖSSBAUER LINESHAPE

A. Energy levels of radioactive paramagnetic ion

Let us consider a Mössbauer nucleus, with an excited state $I(I_z = m)$ and a ground state I_g ($I_{zg} = m_g$), and the Mössbauer transition, with energy $\hbar\Omega$ taking place between I and I_g.

The nuclear states are the eigenvectors of a nuclear Hamiltonian, $\mathcal{H}_N$, such that

$$\begin{aligned} \mathcal{H}_N \, |Im\rangle &= \hbar\Omega \, |Im\rangle \;, \\ \mathcal{H}_N \, |I_g m_g\rangle &= 0 \;. \end{aligned} \tag{1}$$

Let us now assume that the nucleus belongs to a paramagnetic ion embedded in a crystal. The crystal acts on the electronic properties of the ion both through static effects (crystalline field) and through dynamic effects (relaxation).

Concerning static effects, in the case of an iron-group ion, the orbital moment is generally quenched. Then in the lowest (singlet) orbital level, the magnetic hyperfine structure Hamiltonian may be written

$$\begin{aligned} \mathcal{H}_{\text{hyp}} &= \vec{I}\cdot\overleftrightarrow{A}'\cdot\vec{S} \quad \text{(in excited nuclear state)} \;, \\ \mathcal{H}_{\text{hyp}} &= \vec{I}_g\cdot\overleftrightarrow{A}'_g\cdot\vec{S} \quad \text{(in nuclear ground state)} \;. \end{aligned} \tag{2}$$

In addition, both states may exhibit quadrupole effects which we will neglect for the moment. Also both the electronic and nuclear spins may be subjected to a magnetic field. Neglecting the nuclear Zeeman effect, the Zeeman Hamiltonian is

$$\mathcal{H}_Z = \mu_B \vec{H}_0\cdot\overleftrightarrow{g}_e\cdot\vec{S} \;; \tag{3}$$

$\overleftrightarrow{A}'$, $\overleftrightarrow{A}'_g$, and $\overleftrightarrow{g}_e$ often are anisotropic tensors.

Concerning static effects, in the case of a rare-earth ion at low temperatures, we have to consider only the properties of the lowest electronic level arising from the multiplicity J in the crystalline field. If this level is degenerate it may happen that in it, the total electronic angular momentum $\vec{J}$ can be replaced by an effective spin $\vec{S}$ (in cubic symmetry this is possible for the irreducible representations Γ_6, Γ_7, Γ_4, and Γ_5 but not Γ_8). Then $\mathcal{H}_{\text{hyp}}$ and $\mathcal{H}_Z$ also take the same form as Eqs. (2) and (3). In what follows the eigenvalues of S_z will be denoted by μ, μ', ν, and ν'.

In the case of levels Γ_6 or Γ_7 the effective spin is $S=\frac{1}{2}$ and the magnetic hyperfine interaction and Zeeman effect are isotropic

$$\begin{aligned} \mathcal{H}_{\text{hyp}} &= A\,\vec{I}\cdot\vec{S} \;(\text{or } A_g\vec{I}_g\cdot\vec{S})\,, \\ \mathcal{H}_Z &= g\mu_B\,\vec{H}_0\cdot\vec{S}\;. \end{aligned} \tag{4}$$

We will define $\mathcal{H}_0=\mathcal{H}_{\text{hyp}}+\mathcal{H}_Z$; in numerical discussions it will be assumed for convenience that $\mathcal{H}_Z \lesssim \mathcal{H}_{\text{hyp}}$ so that $\mathcal{H}_0 \sim \mathcal{H}_{\text{hyp}}$ (the opposite case $\mathcal{H}_Z \gg \mathcal{H}_{\text{hyp}}$, which is much simpler has already been considered by a number of authors).

It must be borne in mind that the complete static Hamiltonian of the radioactive ion is $\mathcal{H}_0+\mathcal{H}_N$. The levels of this Hamiltonian are schematically represented in Fig. 1.

In order to describe them, we need a complete electronic plus nuclear, or "atomic" basis. The corresponding kets will be denoted by $|Ff\rangle$ for multiplicity F arising from the excited nuclear state I and by $|Gg\rangle$ for multiplicity G arising from the fundamental nuclear state I_g.

B. Relaxation

In addition to splitting the electronic levels, the matrix acts on the ion like a thermal bath (with Hamiltonian $\mathcal{H}_B$) and gives rise to relaxation in and between its electronic levels. The relevant interaction Hamiltonian will be denoted by $\mathcal{H}_1$. Here we shall only be interested in relaxation of the lowest electronic level with effective spin $\vec{S}$. In the coupled electronic plus nuclear scheme, relaxation will take place inside the multiplicities F and G.

What we want to investigate is the effect of this relaxation on the γ-ray emission and absorption between F and G.

C. Mössbauer spectrum

For simplicity let us consider the case of a powder in the absence of external magnetic field, but without excluding the possibility of local magnetic fields with fixed directions with respect to the local crystalline axes.[4] Then, it is possible to show that the Mössbauer intensity at angular frequency $\omega+\Omega$, i.e., at a distance ω from the center of the spectrum, is proportional to[2,5]

$$\begin{aligned} I(\omega) &= \operatorname{Re}F(p) \\ &= \operatorname{Re}\int_0^\infty dt\, e^{-pt}\left(\operatorname{Tr}\left(\sum_M M^\dagger_{LM}(0)\sigma M_{LM}(t)\right)\right)_{\text{av}}\,, \end{aligned} \tag{5}$$

where $p=\frac{1}{2}\Gamma - i\omega$ (Γ is the Mössbauer linewidth); the average is relative to the bath variables and the trace is taken over the atomic variables; $\tilde{M}_L$, with components M_{LM}, is the electromagnetic (elmg) multipole operator associated with the Mössbauer transition assuming pure multipole character, and $\tilde{M}_L(t)$ is the same operator taken in the Heisenberg representation:

$$\begin{aligned} \tilde{M}_L(t) &= \exp\left[(i/\hbar)(\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_B)t\right]\tilde{M}_L \\ &\quad\times\exp\left[-(i/\hbar)(\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_B)t\right] \\ &= U^\dagger(t)\tilde{M}_L U(t)\;. \end{aligned} \tag{6}$$

(We have dropped the nuclear Hamiltonian $\mathcal{H}_N$ which would have the trivial effect of adding the γ transition frequency Ω to the frequencies of the excited states $|Ff\rangle$.)

Finally σ is an atomic density matrix in the normal representation. In an absorption experiment, σ is the equilibrium Boltzmann matrix of level G. In an emission experiment σ is the density matrix of level F, which may or may not be equal to the equilibrium Boltzmann matrix, depending on the radiative feeding and on the rate of thermalization of this level. In the latter case σ might be a function of t.[6]

In practice and in what follows we shall be interested in temperatures which are high compared with the hyperfine coupling A ($A/h \sim 10^2$ to 10^3 MHz $\sim 10^{-2}$ to 10^{-1} K). Then σ is always proportional to the unit matrix and $I(\omega)$ reduces to

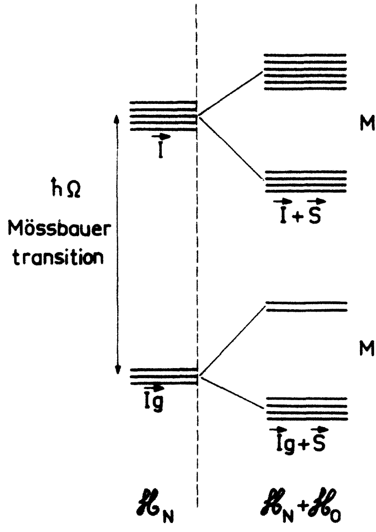

FIG. 1. Schematical representation of the levels of the coupled "electronuclear" system $\mathcal{H}_0+\mathcal{H}_N$.

$$I(\omega)=\mathrm{Re}(F(p))$$

$$=\mathrm{Re}\int_0^\infty dt\,e^{-pt}\sum_{\substack{Mff'\\gg'}}(\langle g|M_{LM}^{\dagger}|f\rangle\langle f|U^{\dagger}(t)|f'\rangle$$

$$\times\langle f'|M_{LM}|g'\rangle\langle g'|U(t)|g\rangle)_{\mathrm{av}}. \tag{7}$$

We see that contrary to what occurs in formulas relative to nonspectroscopic radioactive techniques such as perturbed-angular correlation (PAC) or nuclear orientation (NO),[6] one of the evolution operators $U(t)$ in this formula acts inside the excited nuclear state F, while the other one acts inside the nuclear ground state G.

In Eq. (7) the matrix elements of $\tilde{M}_L$ are known. The computation of the Mössbauer spectrum reduces to a calculation of the average values:

$$(\langle f|U^{\dagger}(t)|f'\rangle\langle g'|U(t)|g\rangle)_{\mathrm{av}}\ , \tag{8}$$

in the presence of hyperfine interactions, local electronic Zeeman effect, and electronic relaxation—the average being taken with respect to the lattice.

D. Liouville formalism

The above formulas can be simplified by resorting to the Liouville formalism. Following Clauser and Blume[1] let us associate with a conventional operator C, the Liouville operator $C^{\times}$, such that

$$C^{\times}B=CB-BC=[C,B]\ , \tag{9}$$

then

$$e^{iC}Be^{-iC}=e^{iC^{\times}}B\ . \tag{10}$$

The Liouville operators associated with Hamiltonians $\mathcal{H}_0$ and $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_B$ will be denoted by $\mathcal{H}_0^{\times}$ and $\mathcal{H}^{\times}$. To the relevant evolution operators $U_0(t)=e^{-i\mathcal{H}_0t/\hbar}$ and $U(t)=\exp[-(i/\hbar)(\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_B)t]$, there corresponds Liouville superoperators $\mathcal{U}_0(t)$ and $\mathcal{U}(t)$. In terms of all these operators, the Heisenberg equation of motion of the elmg multipole moment $\tilde{M}_L$ takes the form

$$\frac{d\tilde{M}_L}{dt}=\frac{i}{\hbar}\mathcal{H}^{\times}\tilde{M}_L\ . \tag{11}$$

Its solution [equivalent to Eq. (6)] is

$$\tilde{M}_L(t)=e^{(i/\hbar)\mathcal{H}^{\times}t}\tilde{M}_L(0)=\mathcal{U}(t)\tilde{M}_L(0) \tag{12}$$

and, after averaging over the lattice, the Mössbauer line shape Eq. (5) is given in terms of the average superoperator $(\mathcal{U}(t))_{\mathrm{av}}$ by

$$I(\omega)=\mathrm{Re}\int_0^\infty dt e^{-pt}\,\mathrm{Tr}\{\tilde{M}_L^{\dagger}\,\sigma(\mathcal{U}(t))_{\mathrm{av}}\tilde{M}_L\}\ . \tag{13}$$

Let us introduce the Laplace transform $(\mathcal{U}(p))_{\mathrm{av}}$ of the superoperator $(\mathcal{U}(t))_{\mathrm{av}}$. Equation (13) becomes

$$I(\omega)=\mathrm{Re}\{\mathrm{Tr}[\tilde{M}_L^{\dagger}\sigma(\mathcal{U}(p))_{\mathrm{av}}\tilde{M}_L]\}\ . \tag{14}$$

Let us now make the "high-temperature" assumption, so that σ is a scalar and make explicit all indices. Then [compare with Eq. (7)],

$$I(\omega)=\mathrm{Re}\sum_M\langle g|M_{LM}^{\dagger}|f\rangle$$

$$\times(\langle fg|\mathcal{U}(p)|f'g'\rangle)_{\mathrm{av}}\langle f'|M_{LM}|g'\rangle\ . \tag{15}$$

This formula shows that the calculation of the Mössbauer spectrum reduces to that of the matrix elements of the Laplace transform of the average evolution superoperator $(\mathcal{U}(t))_{\mathrm{av}}$.

In what follows, we shall find that in the presence of both the static Hamiltonian $\mathcal{H}_0$ and the relaxation, the *average* equation of motion of $\tilde{M}_L$ has the form

$$\frac{d\tilde{M}_L}{dt}=\left(\frac{i}{\hbar}\mathcal{H}_0^{\times}+R\right)\tilde{M}_L\ , \tag{16}$$

which is equivalent to

$$\tilde{M}_L(t)\equiv(\mathcal{U}(t))_{\mathrm{av}}\tilde{M}_L(0)$$

$$=\exp\{[(i/\hbar)\mathcal{H}_0^{\times}+R]t\}\tilde{M}_L(0)\ , \tag{17}$$

where R is a relaxation supermatrix. Taking the Laplace transform of this equation, one finds that

$$(\mathcal{U}(p))_{\mathrm{av}}=[p-(i/\hbar)\mathcal{H}_0^{\times}-R]^{-1}\ . \tag{18}$$

Consequently the problem which we have to solve consists, first in determining the relaxation supermatrix R, second in inverting the supermatrix $p-(i/\hbar)\mathcal{H}_0^{\times}-R$ and finally in applying the result in Eq. (15). Hirst's theory, on the one hand, and Clauser and Blume's theory, on the other hand, differ in the models of electronic relaxation which are used in order to obtain R.

III. SPECIFIC FEATURES OF HIRST'S AND OF CLAUSER AND BLUME'S THEORIES AND COMPARISON BETWEEN THESE THEORIES

A. General formulation of Hirst's theory

The quantity $\tilde{M}_L(t)$ [Eq. (17)] is obtained by solving the equation of motion[7]:

$$\frac{d(\rho\tilde{M}_L)}{dt}=+(i/\hbar)[\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_B,\rho\tilde{M}_L]\ , \tag{19}$$

where ρ is the Boltzmann density matrix of the lattice, under the assumption that $\mathcal{H}_1$ is small (perturbation limit), using the standard approach of relaxation problems as discussed in Chap. VIII of the book by Abragam.[8] In the interaction representation, and after making the usual transformations, Eq. (19) becomes

$$\mathrm{Tr}_{\mathrm{latt}}\left(\frac{d(\rho\tilde{M}_L^{\dagger})}{dt}\right)$$

$$= -\frac{1}{\hbar^2}\int_0^\infty \mathrm{Tr}_{\mathrm{latt}}\{[\mathcal{H}_1^*(t), [\mathcal{H}_1^*(t-\tau), \rho\tilde{M}_L^*(t)]]\}d\tau\ , \tag{20}$$

where the trace is taken over the degrees of freedom of the lattice (bath), which is in thermal equilibrium. The interaction Hamiltonian $\mathcal{H}_1$ between the radioactive atom and the lattice is taken to be

$$\mathcal{H}_1 = \sum_q K^q F^q\ , \tag{21}$$

in which the F^q's are operators involving the bath variables and the dimensionless K^q's involve the electronic variables of the radioactive atom (resonant system). After completing all the calculations and using as basis vectors the eigenvectors of $\mathcal{H}_0$ in order to display the time dependence of the matrix elements, Eq. (20) takes the form {see Refs. 2 [Eq. (4)] and Ref. 7}

$$\frac{d\tilde{M}^*_{fg}}{dt} = \sum_{f'g'} \exp(i(\omega_f - \omega_{f'} - \omega_g + \omega_{g'})t) \times R_{fg,f'g'}\tilde{M}^*_{f'g'} \tag{22}$$

or alternatively in the normal representation the form

$$\frac{d\tilde{M}_{fg}}{dt} = i(\omega_f - \omega_g)\tilde{M}_{fg} + \sum_{f'g'} R_{fg,f'g'}\ \tilde{M}_{f'g'}\ , \tag{23}$$

identical to Eq. (16) as indicated above (the index L has been dropped for simplicity).

As shown by Hirst in Eq. (4) of Ref. 2 the matrix elements $R_{fg,f'g'}$ of the relaxation supermatrix R are linear combinations of the Fourier transforms of the correlation functions associated with the bath variables F^q:

$$R_{fg,f'g'} = \sum_{q,a} r_a J_q(\omega_a, T)\ , \tag{24}$$

in which the circular frequencies ω_a, like $\omega_f - \omega_{f'}$, involve differences between the eigenvalues of Hamiltonian $\mathcal{H}_0$ (which acts *inside* F or G).

Concerning J_q, it has been assumed that for symmetry reasons only the functions

$$J_{qq'}(\omega, T) \equiv \frac{1}{\hbar^2}\int_{-\infty}^{+\infty} d\tau\, e^{-i\omega\tau}\mathrm{Tr}_{\mathrm{latt}}[\rho F^{q'*}(0)F^{q*}(\tau)]$$

$$\equiv \frac{1}{\hbar^2}\int_{-\infty}^{+\infty} d\tau\, e^{-i\omega\tau}(F^{q'*}(0)F^{q*}(\tau))_{\mathrm{av}} \tag{25}$$

for which $q' = -q$, are different from zero $[J_q(\omega, T) \equiv J_{q_1 -q}(\omega, T)]$.

The lattice Boltzmann equilibrium implies that

$$J_{-q}(-\omega, T) = e^{-\hbar\omega/k_B T} J_q(\omega, T)\ . \tag{26}$$

In the high-temperature approximation ($\mathcal{H}_0/k_B T \ll 1$), the exponential factor reduces to unity.

B. Validity of Hirst's equations

As discussed by Abragam[8] the condition for the validity of the perturbation method used by Hirst is that

$$(\mathcal{H}_1^2/\hbar^2)\tau_c^2 \sim (\langle F^2\rangle/\hbar^2)\tau_c^2 \ll 1 \tag{27}$$

or alternatively, since $R_{fg,f'g'} \sim J_q(\omega, T) \sim \langle F^2/\hbar^2\rangle\tau_c$,

$$R \ll 1/\tau_c\ , \tag{28}$$

where τ_c is some characteristic time associated with the lattice fluctuations.

When $\mathcal{H}_1$ is a true random function of time as in most of Chap. VIII of Ref. 8, τ_c is the correlation time of the random function. When the bath quantum variables are made explicit and $\mathcal{H}_1$ does not contain the time explicitly, as in the case here, $\tau_c \sim \hbar n(E)$ where $n(E)$ is the density of states of the lattice which comes into play when one averages over the bath variables in expressions such as Eq. (25). As an example, for electronic relaxation by the conduction electrons (see Sec. IV), $\tau_c \sim \hbar/E_F$ (Ref. 8, p. 357).

On the other hand, in relaxation theories one often makes the "secular approximation" which consists in neglecting all the terms in the right-hand side of Eq. (22) for which

$$\omega_f - \omega_{f'} - \omega_g + \omega_{g'} \neq 0\ .$$

This approximation is valid under the condition that

$$R \ll \omega_f - \omega_{f'} - \omega_g + \omega_{g'} \quad \text{or} \quad R \ll \mathcal{H}_0/\hbar$$

and corresponds to a situation where the broadening of the lines of the spectrum due to relaxation is small compared with the intervals between these lines.

But the secular approximation is not necessary, and we will take advantage of this fact since we are interested in situations where the Mössbauer spectrum coalesces, i.e., for which $R \sim \mathcal{H}_0/\hbar$.

Assuming that in the region of greatest physical interest $\frac{1}{10}\mathcal{H}_0 \lesssim \hbar R \lesssim 10\mathcal{H}_0$ then in this range, condition (28) for the validity of perturbation theory and therefore of Hirst's theory can also be written

$$(1/\hbar)\mathcal{H}_0 \ll (1/\tau_c)\ . \tag{29}$$

$\mathcal{H}_0$ is of the order of the hyperfine structure, i.e., $\mathcal{H}_0/h \sim 10^2$ to 10^3 MHz.

Thus the condition for the validity of Hirst's theory in the domain where the spectrum coalesces is that $\tau_c \ll 10^{-10}$ sec where τ_c is the correlation time of the relaxation Hamiltonian acting on the electronic variables (in practice on the spin $\vec{S}$). Typical correlation times of a lattice bath are of order 10^{-12} sec or less; it follows that this condition is not very restrictive.[9]

As pointed out by Hirst[2] in many previous theories one did not treat the coupled electronic and nuclear moments as a single quantum-mechanical resonant system. Instead the nuclear spin was singled out and considered as being submitted to a fluctuating electronic spin $\vec{S}$. In these conditions the Hamiltonian responsible for relaxation was no longer $\mathcal{H}_1$, but rather $\mathcal{H}_0$ itself and the correlation time associated with this Hamiltonian was not τ_c but instead T_1, the relaxation time of the electronic spin. The condition for the validity of perturbation theory was that $(\mathcal{H}_0^2/\hbar^2)T_1^2 \ll 1$, instead of $(\mathcal{H}_1^2/\hbar^2)\tau_c^2 \ll 1$ or equivalently $\mathcal{H}_0/\hbar\tau_c \ll 1$ [see Eq. (29) above]. But $T_1 \sim 1/R$ (see below) is much longer than τ_c, since $R \ll 1/\tau_c$ [Eq. (28)] and thus is much more likely to become of the order of $\hbar/\mathcal{H}_0$ at low temperatures. In this case (precisely in the most interesting region), these previous perturbation theories[10] were no longer valid and one had to resort to stochastic theories.

Spherical relaxation. In many problems it is convenient to assume "spherical relaxation," i.e.,[11]

$J_q(\omega_a, T)$ independent of ω_a: extreme narrowing,

$J_q(\omega_a, T)$ independent of q, i.e., "spherical symmetry".

As shown by Eq. (26) or by application of the fluctuation-dissipation theorem, the first of these two conditions implies that $\hbar\omega_a/k_BT \ll 1$ or $\mathcal{H}_0/k_BT \ll 1$: This is the high-temperature assumption; when it is satisfied and when inequality (29) is fulfilled, extreme narrowing is automatically realized.[12] The second condition implies that the instantaneous fluctuations associated with $\mathcal{H}_1$ are isotropic.

C. Application of Hirst's theory to relaxation caused by fluctuating magnetic field acting on electronic spin

Let us assume that inside the atomic F and G levels relaxation proceeds through the coupling of $\vec{S}$ with a fluctuating field, $\vec{H}$:

$$\mathcal{H}_1 = g\mu_B \vec{S}\cdot\vec{H} \,, \tag{30}$$

and that the conditions for "spherical relaxation" are fulfilled. Then Eq. (20) can be written

$$\frac{d\tilde{M}_L^*}{dt} = -\frac{1}{\hbar^2}\int_0^\infty d\tau\,\big([g\mu_B\vec{H}^*(t)\cdot\vec{S}^*(t)\,,\,[g\mu_B\vec{H}^*(t-\tau)\cdot\vec{S}^*(t-\tau),\,\tilde{M}_L^*(t)]]\big)_{\text{av}} \,, \tag{31}$$

and the matrix elements of the supermatrix R, which enters Eqs. (22) and (23), are found to be

$$R_{fg,f'g'} = \tfrac{1}{2}g^2J(T)\Big(-2S(S+1)\delta_{ff'}\delta_{gg'} + 2\sum_{j=x,y,z}\langle f|S_j|f'\rangle\langle g'|S_j|g\rangle\Big) \,, \tag{32}$$

with

$$\tfrac{1}{2}g^2J(T) = \frac{g^2\mu_B^2}{2\hbar^2}\int_{-\infty}^{+\infty}(H_z^*(0)H_z^*(-\tau))_{\text{av}}\,d\tau \,. \tag{33}$$

Since $\vec{S}$ only operates on the electronic variables, this may also be written, using as basis vectors the eigenvectors of $\vec{S}^2$, $\vec{I}^2$, $\vec{I}_g^2$, S_z, I_z, I_{zg}:

$$\langle Im\,S\nu,\,I_gm_gS\mu|R|Im'S\nu',\,I_gm_g'S\mu'\rangle = \delta_{mm'}\delta_{m_gm_g'}\tfrac{1}{2}g^2J(T)\Big(-2S(S+1)\delta_{\mu\mu'}\delta_{\nu\nu'} + 2\sum_j\langle\nu|S_j|\nu'\rangle\langle\mu'|S_j|\mu\rangle\Big) \,. \tag{34}$$

As shown by Eqs. (32) and (34) the relaxation matrix depends on only one parameter $\frac{1}{2}g^2J(T)$. In order to find its physical significance, let us investigate what the relaxation equation of $\langle S_z\rangle$ would be in the absence of hyperfine coupling. Dropping this coupling in $\mathcal{H}_0$, the equation may be written in the interaction representation as

$$\frac{d\langle S_z^*\rangle}{dt} = -\frac{1}{\hbar^2}\int_0^\infty d\tau(\langle[\mathcal{H}_1^*(t),\,[\mathcal{H}_1^*(t-\tau),\,S_z^*]]\rangle)_{\text{av}} \,, \tag{35}$$

where a double average is taken, on the lattice bath and on the density matrix of the electronic spin. After completing all the calculations, and under the assumptions of spherical relaxation, we find that

$$\frac{d\langle S_z\rangle}{dt} = -g^2J(T)\langle S_z\rangle \,. \tag{36}$$

Therefore, by identification with the standard definition of the longitudinal relaxation time T_1 of the electronic spin,

$$g^2J(T) = 1/T_1 \,. \tag{37}$$

Note that, for a spin $\frac{1}{2}$, one also has, in terms of the transition probabilities W,

$$1/T_1 = W_{1/2\to-1/2} + W_{-1/2\to1/2} \,, \tag{38}$$

which at high temperatures reduces to $1/T_1 = 2W$. Consequently, when $S=\frac{1}{2}$,

$$\tfrac{1}{2}g^2J(T) = W \,. \tag{39}$$

Before applying the preceding results [Eq. (34)] to the computation of the Mössbauer line shape, we shall compare them with the theory of Clauser and Blume.

D. Clauser and Blume's theory

We have seen in Eqs. (14) and (15) that the Mössbauer line shape is related to the Laplace transform $(\mathcal{U}(p))_{\mathrm{av}}$ of the average evolution superoperator $(\mathcal{U}(t))_{\mathrm{av}}$.

In Clauser and Blume's theory the relaxation Hamiltonian is assumed to consist in a sum of random independent pulses acting on the electronic spin:

$$\mathcal{H}_1(t) = \hbar \sum_i V_i \delta(t - t_i) \ . \tag{40}$$

To each of these, there corresponds a transition operator;

$$T_i = e^{-iV_i} \ . \tag{41}$$

Then, after n pulses in a time interval t, the usual evolution operator is

$$U(t) = U_0(t - t_n) T_n \cdots T_1 U_0(t_1) \ . \tag{42}$$

The probability that n pulses take place during this time interval is given by a Poisson distribution,

$$P_n(t) = [(\lambda t)^n / n!]\, e^{-\lambda t} , \tag{43}$$

where λ is the mean frequency of the pulses. Blume and Clauser resort to the Liouville formalism ($\mathcal{H}_0 \to \mathcal{H}_0^\times$, $V_i \to V_i^\times$, and $U \to \mathcal{U}$). They also introduce an average transition operator (averaged over the type of pulses),

$$\mathcal{T}_{\mathrm{av}} = (e^{-iV_i^\times})_{\mathrm{av}} \tag{44}$$

and define a relaxation supermatrix,

$$\mathcal{W} = \lambda(\mathcal{T}_{\mathrm{av}} - 1) \ . \tag{45}$$

In terms of these, they find that the Laplace transform of the evolution superoperator $\mathcal{U}_{\mathrm{av}}$ which enters the expression of the Mössbauer line shape is

$$(\mathcal{U}(p))_{\mathrm{av}} = [p - (i/\hbar)\mathcal{H}_0^\times - \mathcal{W}]^{-1} \ . \tag{46}$$

In this case too $(\mathcal{U}(p))_{\mathrm{av}}$ has the form of Eq. (18).

It now remains to make explicit the relaxation mechanism and the matrix $\mathcal{W}$. In Chap. III of their paper, Blume and Clauser consider pulses of the form

$$V_i = \vec{\mathrm{h}}_i \cdot \vec{\mathrm{S}} = |h| \vec{\mathrm{u}} \cdot \vec{\mathrm{S}} , \tag{47}$$

where the direction $\vec{\mathrm{u}}$ and length $|h|$ of the fictitious dimensionless field $\vec{\mathrm{h}}$ are independent random variables. Then,

$$T_i = e^{-i\vec{\mathrm{h}}_i \cdot \vec{\mathrm{S}}} \ . \tag{48}$$

In the particular case of a spin $S = \frac{1}{2}$ and assuming isotropic pulses, if one defines the average values over the pulse intensity $|\vec{\mathrm{h}}_i|$,

$$x = (\sin^2 \tfrac{1}{2}h)_{\mathrm{av}} \ , \quad 1 - x = (\cos^2 \tfrac{1}{2}h)_{\mathrm{av}} \ , \tag{49}$$

it is easy to see that the relaxation matrix W, when referred to the basis states $|S, S_z\rangle$, takes the form [Eqs. (25) and (34c) of Ref. 1]

$$\langle \mu\nu | \mathcal{W} | \mu'\nu' \rangle = \tfrac{2}{3} x\lambda \Big(-\tfrac{3}{2} \delta_{\mu\mu'} \delta_{\nu\nu'} + 2 \sum_j \langle \nu | S_j | \nu' \rangle \langle \mu' | S_j | \mu \rangle \Big) \ . \tag{50}$$

It appears that this matrix is formally identical to Hirst's matrix R [Eq. (34)] apart from the replacement of

$$\tfrac{1}{2} g^2 J(T) \ \text{by} \ \tfrac{2}{3} x\lambda \ .$$

And in this case too, the factor in front of the brackets [Eq. (50)], i.e., $\frac{2}{3} x\lambda$, can be interpreted as one-half the inverse relaxation time of the electronic spin $\vec{\mathrm{S}}$: Indeed it has been noted by Clauser and Blume that $W \equiv \frac{2}{3} x\lambda$ is the probability that one pulse produces a flip of $\vec{\mathrm{S}}$ from $+\frac{1}{2}$ to $-\frac{1}{2}$. But we have recalled that for a spin $S = \frac{1}{2}$, $\frac{1}{2} T_1 = W$. Therefore, in this theory

$$1/T_1 = \tfrac{4}{3} x\lambda \ . \tag{51}$$

We must now investigate why—at least for $S = \frac{1}{2}$—Hirst's matrix R and Clauser and Blume's matrix $\mathcal{W}$ are equivalent, except for the microscopic interpretation of the multiplicative factor.

E. Comparison between Hirst's theory and Clauser and Blume's theory

It is easy to demonstrate that for *small* $|h|$, the theory of Clauser and Blume must lead to a relaxation matrix formally identical to that obtained by application of Hirst's theory (Sec. III C) *whatever* S. In addition for $S = \frac{1}{2}$, this identity remains true whatever h.

Let us first consider the case of arbitrary S. In the stochastic approach the variation of $\tilde{M}_L$ during one pulse $\vec{\mathrm{h}} \cdot \vec{\mathrm{S}}$ is given by

$$\Delta \tilde{M}_L = e^{i\vec{\mathrm{h}} \cdot \vec{\mathrm{S}}} \tilde{M}_L e^{-i\vec{\mathrm{h}} \cdot \vec{\mathrm{S}}} - \tilde{M}_L \ . \tag{52}$$

With an average number λ of pulses per unit time, the variation of $\tilde{M}_L$ due to relaxation is

$$\left(\frac{d\tilde{M}_L}{dt} \right)_{\mathrm{relax}} = \lambda \Delta \tilde{M}_L = \lambda (e^{i\vec{\mathrm{h}} \cdot \vec{\mathrm{S}}} \tilde{M}_L e^{-i\vec{\mathrm{h}} \cdot \vec{\mathrm{S}}} - \tilde{M}_L) \ . \tag{53}$$

Let us now assume that $|\vec{\mathrm{h}}_{\mathrm{av}}| \ll 1$. Then it is possible to expand the exponential factors and, taking into account the fact that $\vec{\mathrm{h}}_{\mathrm{av}} = 0$, we find

$$\left(\frac{d\tilde{M}_L}{dt} \right)_{\mathrm{relax}} = -\tfrac{1}{2} \lambda ([\vec{\mathrm{h}} \cdot \vec{\mathrm{S}}, [\vec{\mathrm{h}} \cdot \vec{\mathrm{S}}, \tilde{M}_L]])_{\mathrm{av}}$$

$$= -\tfrac{1}{2} \lambda \langle h^2 \rangle_{\mathrm{av}} ([\vec{\mathrm{u}} \cdot \vec{\mathrm{S}}, [\vec{\mathrm{u}} \cdot \vec{\mathrm{S}}, \tilde{M}_L]])_{\mathrm{av}} \ . \tag{54}$$

By comparison, in Hirst's approach we have found [Eq. (31)]

$$\left(\frac{d\tilde{M}_L}{dt} \right)_{\mathrm{relax}}$$

$$= -\frac{g^2\mu_B^2}{\hbar^2}\int_0^\infty d\tau\,([\vec{\mathrm{H}}(0)\cdot\vec{\mathrm{S}},[\vec{\mathrm{H}}(-\tau)\cdot\vec{\mathrm{S}},\tilde{M}_L]])_{\mathrm{av}}. \tag{55}$$

We see that the same double commutator occurs in both cases. Therefore, assuming isotropic pulses in the first case and spherical relaxation in the second case, one may expect to get the same relaxation matrix apart from a multiplicative factor which is equal to $\frac{1}{2}\lambda(\frac{1}{3}\langle h^2\rangle)$ or $\frac{1}{2}g^2J(T)$, respectively.

In the particular case of a spin $S=\frac{1}{2}$, the formal identity of the two matrices remains true whatever $|\vec{\mathrm{h}}|$. This stems from the fact that in this case we have the identity

$$e^{-i\vec{\mathrm{h}}\cdot\vec{\mathrm{S}}}=\cos\tfrac{1}{2}h-2(i\sin\tfrac{1}{2}h)\vec{\mathrm{u}}\cdot\vec{\mathrm{S}}\;. \tag{56}$$

Hence dropping linear terms in $\vec{\mathrm{u}}$, which vanish upon averaging,

$$\Delta\tilde{M}_L=(\sin^2\tfrac{1}{2}h)[-\tilde{M}_L+4(\vec{\mathrm{u}}\cdot\vec{\mathrm{S}})\tilde{M}_L(\vec{\mathrm{u}}\cdot\vec{\mathrm{S}})]\;. \tag{57}$$

It is seen that the second-order polynomial in $\vec{\mathrm{S}}$ which appears in the bracket does not depend on the strength of h. Equivalently, after averaging, Eq. (53) is found to be replaced by

$$\frac{d\tilde{M}_L}{dt}=-2\lambda(\sin^2\tfrac{1}{2}h)_{\mathrm{av}}([\vec{\mathrm{u}}\cdot\vec{\mathrm{S}},[\vec{\mathrm{u}}\cdot\vec{\mathrm{S}},\tilde{M}_L]])_{\mathrm{av}}\;, \tag{58}$$

which still contains the same double commutator as Eq. (54) so that proportionality remains true, with a multiplicative factor $\frac{2}{3}\lambda(\sin^2\frac{1}{2}h)_{\mathrm{av}}=\frac{2}{3}x\lambda$, as found above. This result is clearly due to the fact that $e^{-i\vec{\mathrm{h}}\cdot\vec{\mathrm{S}}}$ is linear in S when $S=\frac{1}{2}$.

But this simple property does not hold for general spin. Indeed it has been established that[13]

$$e^{-ih\vec{\mathrm{u}}\cdot\vec{\mathrm{S}}}=4\pi\sum_{L=0}^{2S}\frac{(i)^L f_L(hS)}{[2(2L+1)]^{1/2}}\,Y_L(\vec{\mathrm{u}})\cdot T_L(S)\;. \tag{59}$$

This expansion is a polynomial in S of degree $2S$, which becomes linear in S only for small h. One must however point out (Blume, private communication) that this limitation could, in principle, be circumvented by using for V_i a more general expression of the following type:

$$V_i=\sum_{L=1}^{2S}a_L Y_L(i)T_L(S)\;.$$

In this case, the complete equivalence of the Hirst-Clauser and the Blume theories would follow whatever S.

F. Microscopic interpretation of multiplicative factor

We have found that for a spin $S=\frac{1}{2}$ in the presence of a random field, in both Hirst's and Clauser and Blume's theories the multiplicative factor in front of the relaxation matrix must be identified with $\frac{1}{2}T_1$, where T_1 is the longitudinal relaxation time of the electronic spin S [in Hirst's case (Sec. III C) this is true whatever S]. It now remains to relate T_1 to the microscopic mechanisms which are responsible for the electronic relaxation.

In solids the interactions that cause relaxation are usually described either classically as random stationary fluctuating couplings or quantum mechanically as couplings with a bath having a continuous final density of states. In both eventualities this coupling acts continuously on the electronic system. Hirst's model, which corresponds to a continuous disturbance appears to be well suited to handling such couplings. On the other hand, stochastic models which assume discontinuous pulses, are better adapted to collision problems in gases. In this last case, assuming λ collisions per unit time, during each of which the atom is submitted to a transient Hamiltonian $\mathcal{H}_1$, the equation of motion of the density matrix generally may be written (assuming for simplicity that $\mathcal{H}_1$ is small[14])

$$\left(\frac{d\sigma}{dt}\right)_{\mathrm{coll}}=-\frac{\lambda}{\hbar^2}\int_{-\infty}^{+\infty}dt'\int_{-\infty}^{t'}dt''$$

$$\times([\mathcal{H}_1(t'),[\mathcal{H}_1(t''),\sigma(t)]])_{\mathrm{av}}\;. \tag{60}$$

For constant pulses of intensity $\mathcal{H}_1$ and length $\mathcal{T}_c$,

$$\left(\frac{d\sigma}{dt}\right)_{\mathrm{coll}}=-\frac{\lambda}{\hbar^2}\frac{\mathcal{T}_c'^2}{2}[\mathcal{H}_1,[\mathcal{H}_1,\sigma]]\;. \tag{61}$$

Clauser and Blume's limiting case [Eq. (54)] is obtained by taking $\mathcal{H}_1/\hbar=(\vec{\mathrm{h}}\cdot\vec{\mathrm{S}}/\mathcal{T}_c')$ and making $\mathcal{T}_c'$ go to zero.

It is difficult to establish a connection between such a model and real phenomena taking place in solids. For this reason, whenever a detailed microscopic interpretation of the relaxation rates will be needed, Hirst's approach seems to be preferable, inasmuch as its conditions of validity are not very restrictive. A final remark should however be made. Prior to Hirst's theory, there had been some attempts to solve the problem of relaxation effects in Mössbauer spectra along the same lines,[5] but in the absence of any definite model of electronic relaxation these treatments remained purely formal. Hirst made major progress by applying his formulas to a simple case of spherical relaxation, where the relaxation matrix can be entirely calculated and expressed in terms of a single parameter. By comparison, in the most general case, the super-relaxation-matrix of an electronic spin $\frac{1}{2}$ without hyperfine coupling is a function of nine parameters which are *a priori* unknown; if, in addition, this spin is coupled with a nuclear spin, at low temperatures where the $J_q(\omega_a, T)$ depend on ω_a, the relaxation matrix in the coupled $(\vec{\mathrm{I}},\vec{\mathrm{S}})$ scheme may involve still more unknown parameters. For this reason the detailed interpretation of relaxation effects in Mössbauer spectra using Hirst's theory is restricted to cases where the relaxation mechanism is perfectly known in order that the relaxation supermatrix can be entirely calculated and expressed as a function of a very small number of unknown parameters.

IV. APPLICATION OF HIRST'S THEORY TO MÖSSBAUER TRANSITION $0^+ \to 2^+$, IN PRESENCE OF HYPERFINE COUPLING WITH ELECTRONIC SPIN $S=\frac{1}{2}$ SUBJECT TO RELAXATION

A. Formulation of problem

Mössbauer transitions $0^+ \to 2^+$ ($I_g=0$, $I=2$) are frequently encountered in the even-even nuclei of the rare-earth series. For such transitions Eq. (15) (relative to the Mössbauer spectrum of a powder) may be put into the form

$$
\begin{aligned}
I(\omega) &= \mathrm{Re}F(p) \\
&= \mathrm{Re} \sum_{m,\mu,\mu'} \sum_{M} \langle I_g=0,0 | M^\dagger_{LM} | Im\rangle\langle Im' | M_{LM} | I_g=0,0\rangle \\
&\quad \times \langle (ImS\mu),(I_g=0,0,S\mu) | (\mathfrak{U}(p))_{\mathrm{av}} \\
&\quad \times | (Im'S\mu'),(I_g=0,0,S\mu')\rangle . \qquad (62)
\end{aligned}
$$

But by virtue of Edmonds [Ref. 15, Eq. (3.5.4)],

$$
\begin{aligned}
&\sum_{M} \langle I_g=0,0 | M^\dagger_{LM} | Im\rangle\langle Im' | M_{LM} | I_g=0,0\rangle \\
&\quad = \delta_{mm'} \times \mathrm{const}; \qquad (63)
\end{aligned}
$$

the constant being independent of m. Then, within a constant factor;

$$
\begin{aligned}
I(\omega) = \mathrm{Re} \sum_{m\mu\mu'} &\langle (ImS\mu)(0,0,S\mu) | (\mathfrak{U}(p))_{\mathrm{av}} \\
&\times | (ImS\mu')(0,0,S\mu')\rangle , \qquad (64)
\end{aligned}
$$

in which $(\mathfrak{U}(p))_{\mathrm{av}} = 1/(p - R - (i/\hbar)\mathcal{H}_0^\times)$.

We must evaluate $(\mathfrak{U}(p))_{\mathrm{av}}$ in the presence of electronic relaxation. Up to now we have considered the case of an isotropic hyperfine interaction $\mathcal{H} = A\vec{I}\cdot\vec{S}$ and assumed a relaxation Hamiltonian of the form $\mathcal{H}_1 = g\mu_B\vec{H}\cdot\vec{S}$. Note that $\mathcal{H}_1$ may represent either relaxation due to a real magnetic field or, alternatively, by virtue of the properties of the Pauli matrices, any type of relaxation process, provided the quantities $J_q(\omega, T)$ which enter R are adequately adjusted.

In the present chapter we will consider the case of axial symmetry. We write the hyperfine interaction as

$$\mathcal{H}_{\mathrm{hf}} = A_\parallel I_z S_z + A_\perp (I_x S_x + I_y S_y) + \beta[3I_z^2 - I(I+1)] , \qquad (65)$$

where we have allowed for a possible quadrupole effect $[\beta = eQV_{zz}/4I(2I-1)]$. The local electronic Zeeman effect, if any, will be represented by

$$\mathcal{H}_Z = \alpha S_z . \qquad (66)$$

In the relaxation Hamiltonian, we want to take account of the uniaxial symmetry, but at the same time to keep the extreme narrowing assumption.

The simplest way to do this consists in writing

$$\mathcal{H}_1 = g'_\parallel \mu_B H_z S_z + g'_\perp \mu_B (H_x S_x + H_y S_y) , \qquad (67)$$

with the convention that all the quantities $J_q(\omega, T)$ associated with H^+, H^-, H_z *in the coupled IS scheme* are taken to be equal to a constant $J(T)$, the departure from isotropy being entirely included in the apparent Landé factors $g'_\parallel$ and $g'_\perp$ (which will generally differ from the real Landé factors $g_\parallel$ and $g_\perp$). Let us now define $W_\parallel$ and $W_\perp$:

$$W_\parallel = \tfrac{1}{2} g'^2_\parallel J , \quad W_\perp = \tfrac{1}{2} g'^2_\perp J . \qquad (68)$$

In terms of these two parameters Hirst's matrix becomes [compare with Eq. (34)]

$$
\begin{aligned}
&\langle m\nu, 0\mu | R | m'\nu', 0\mu'\rangle \\
&\quad = \delta_{mm'} [\delta_{\mu\mu'}\delta_{\nu\nu'}(-\tfrac{1}{2} W_\parallel - W_\perp) + 2W_\parallel \langle \nu | S_z | \nu'\rangle \\
&\qquad \times \langle \mu' | S_z | \mu\rangle + W_\perp (\langle \nu | S_+ | \nu'\rangle\langle \mu' | S_- | \mu\rangle \\
&\qquad + \langle \nu | S_- | \nu'\rangle\langle \mu' | S_+ | \mu\rangle)] . \qquad (69)
\end{aligned}
$$

As concerns the parallel with the theory of Clauser and Blume it is interesting to note that the matrices represented in Tables I and II of their article correspond, respectively, to $W_\parallel = 0$, $W_\perp = \lambda$ and to $W_\parallel = W_\perp (= \frac{2}{3} x\lambda)$.

The two-parameters expression (69) for R is more general; as a matter of fact, within the extreme narrowing assumption, it represents the most general relaxation matrix in axial symmetry for an electronic doublet exhibiting hyperfine structure. Note that $W_\perp$ and $W_\parallel$ are related to the longitudinal and transverse relaxation times T_1 and T_2 of the electronic spin by

$$1/T_1 = 2W_\perp , \quad 1/T_2 = W_\perp + W_\parallel . \qquad (70)$$

B. Computation of Mössbauer line shape

We must compute the matrix

$$\mathcal{V}(p) = p - R - (i/\hbar)\mathcal{H}_0^\times , \qquad (71)$$

and invert it. We will find that the matrix $\mathcal{V}(p)$ factors into submatrices of low dimensionality, so that the calculation can be performed algebraically.

The general matrix element of $\mathcal{V}(p)$ is

$$
\begin{aligned}
&\langle (ImS\nu)(00S\mu) | \mathcal{V}(p) | (Im'S\nu')(00S\mu')\rangle \\
&\quad \equiv \langle \mu\nu m | \mathcal{V}(p) | \mu'\nu' m\rangle . \qquad (72)
\end{aligned}
$$

The dimension of this matrix is $(2I+1)(2S+1)^2 \times (2I+1)(2S+1)^2$, i.e., since $I=2$ and $S=\frac{1}{2}$, the dimension of the matrix is 20×20.

It is clear that

$$\langle \mu\nu m|p|\mu'\nu'm'\rangle = \delta_{\mu\mu'}\delta_{\nu\nu'}\delta_{mm'}p\ . \tag{73}$$

Also we have seen that, since the relaxation matrix operates only on the electronic spin

$$\langle \mu\nu m|R|\mu'\nu'm'\rangle = \delta_{mm'}R_{\mu\nu,\mu'\nu'}\ , \tag{74}$$

in which $R_{\mu\nu,\mu'\nu'}$ is given by the bracket of Eq. (69). One notes that its only nondiagonal matrix elements are such that $\mu = \nu$ and $\mu' = \nu'$.

As regards the matrix elements of $\mathcal{H}_0^\times$, after relation (28) of Ref. 1,

$$\begin{aligned}\langle \mu\nu m|\mathcal{H}_0^\times|\mu'\nu'm'\rangle &= \delta_{\nu\nu'}\delta_{mm'}\langle \mu|\mathcal{H}_0|\mu'\rangle\\ &\quad -\delta_{\mu\mu'}\langle \nu'm'|\mathcal{H}_0|\nu m\rangle\ ,\end{aligned}$$

$\langle \mu|\mathcal{H}_0|\mu'\rangle = \alpha\delta_{\mu\mu'}\mu$ (local Zeeman effect in the ground state). In the excited state inspection of Eq. (69) shows that $\langle \nu'm'|\mathcal{H}_0|\nu m\rangle$ is nonzero only if $\nu' + m' = \nu + m$.

From all the preceding remarks, it follows that if we consider the set of states $|f(m)\rangle = |++, m\rangle$, $|--, m\rangle$, $|-+, m-1\rangle$, and $|+-, m+1\rangle$, $\mathcal{V}(p)$ has no matrix elements between states belonging to two different sets, i.e.,

$$\langle f(m)|\mathcal{V}(p)|f(m')\rangle = 0 \ \text{ if } \ m' \neq m\ . \tag{75}$$

Therefore the matrix $\mathcal{V}(p)$ factors into seven submatrices: two 1×1 matrices [sets $f(3)$ and (-3), reducing to $|-,+,2\rangle$ and $|+,-,-2\rangle$], two 3×3 matrices [sets $f(2)$ and $f(-2)$], and three 4×4 matrices [sets $f(1)$, $f(-1)$, $f(0)$]. Furthermore, in the absence of local Zeeman effects, the matrices for $f(m)$ and $f(-m)$ are identical for each m, so we need consider only four different matrices.

We now must invert these matrices. But in virtue of Eq. (64) we only need the matrix elements

$$\begin{aligned}&\langle \mu\mu m|\mathcal{V}^{-1}(p)|\mu'\mu'm\rangle\\ &\quad\equiv \langle \mu\mu m|(\mathcal{V}(p))_{\text{av}}|\mu'\mu'm\rangle\ ,\end{aligned}$$

i.e., four elements for each of the matrices of dimension higher than 1. Taking symmetry into account, it is sufficient to calculate nine of them.

C. Results of calculations and discussion: (Mössbauer spectrum of a powder)

After completing the calculations the expression of the line shape in the case of a *powder* spectrum is found to be $I(\omega) = \text{Re}[F(p)]$ with

$$F(p) = \frac{A}{B} + \frac{A'}{B'} + \frac{C}{D} + \frac{C'}{D'} + \frac{E}{F}\ , \tag{76}$$

in which (expressing $\mathcal{H}_0$ in angular frequency units)

$$\begin{aligned}
A &= 2[p + W_\parallel + W_\perp + i(\tfrac{1}{2}A_\parallel + \alpha - 3\beta)](p + 2W_\perp + 6i\beta) + A_\perp^2\ ,\\
B &= [p + W_\parallel + W_\perp + i(\tfrac{1}{2}A_\parallel + \alpha - 3\beta)][(p + W_\perp + 6i\beta)^2 + A_\parallel^2 - W_\perp^2] + A_\perp^2[p + W_\perp + i(A_\parallel + 6\beta)]\ ,\\
C &= [p + W_\parallel + W_\perp + i(-A_\parallel - \alpha + 6\beta)]\{2[p + W_\parallel + W_\perp + i(\alpha - 6\beta)](p + 2W_\perp - 3i\beta) + \tfrac{3}{2}A_\perp^2\} + A_\perp^2[p + W_\parallel + W_\perp + i(\alpha - 6\beta)]\ ,\\
D &= [p + W_\parallel + W_\perp + i(-A_\parallel - \alpha + 6\beta)]\{\tfrac{3}{2}A_\perp^2[p + W_\perp + i(\tfrac{1}{2}A_\parallel - 3\beta)] + [(p + W_\perp - 3i\beta)^2 + \tfrac{1}{4}A_\parallel^2 - W_\perp^2]\\
&\quad \times [p + W_\parallel + W_\perp + i(\alpha - 6\beta)]\} + [p + W_\parallel + W_\perp + i(\alpha - 6\beta)][p + W_\perp + i(-\tfrac{1}{2}A_\parallel - 3\beta)]A_\perp^2 + \tfrac{3}{2}A_\perp^4\ ,\\
E &= 3A_\perp^2[p + W_\parallel + W_\perp + i(-\tfrac{1}{2}A_\parallel - 3\beta)] + 2(p + 2W_\perp - 6i\beta)\{[p + W_\parallel + W_\perp + i(\tfrac{1}{2}A_\parallel - 3\beta)]^2 + \alpha^2\}\ ,\\
F &= 3A_\perp^2(p + W_\perp - 6i\beta)[p + W_\parallel + W_\perp + i(-\tfrac{1}{2}A_\parallel - 3\beta)] + [(p + W_\perp - 6i\beta)^2 - W_\perp^2]\{[p + W_\parallel + W_\perp + i(-\tfrac{1}{2}A_\parallel - 3\beta)]^2\\
&\quad + \alpha^2\} + \tfrac{9}{4}A_\perp^4\ .
\end{aligned} \tag{77}$$

In this formula, $p = \frac{1}{2}\Gamma - i\omega$, and A', B', C', and D' are deduced from A, B, C, and D by replacing α by $-\alpha$. Let us recall that this expression being relative to a powder spectrum, the electronic Zeeman Hamiltonian αS_z must represent the effect of a molecular field parallel to the local Oz axis for each crystallite, and not the effect of an external magnetic field.

Particular cases

a. Cubic symmetry. Here[16] $W_\parallel = W_\perp = W$, $A_\perp = A_\parallel = A$, and $\beta = 0$. In the absence of electronic Zeeman effect ($\alpha = 0$), and in the slow relaxation limit ($W = 0$) the spectrum consists of an asymmetric doublet:

$$F(p) = \frac{6}{p + iA} + \frac{4}{p - \frac{3}{2}iA}\ . \tag{78}$$

This doublet corresponds to the eigenvalues $F = \frac{5}{2}$ and $\frac{3}{2}$ of the total angular momentum $\vec{F} = \vec{I} + \vec{S}$ ($I = 2$, $S = \frac{1}{2}$), i.e., to the eigenvalues $E = A$ and $E = -\frac{3}{2}A$ of the hyperfine Hamiltonian $\mathcal{H} = A\vec{I}\cdot\vec{S}$.

b. Extreme anisotropy. Here $A_\perp = 0$. This is the effective-field case. Neither $W_\parallel$ nor α appear in $F(p)$ which is given by

$$\tfrac{1}{4}F(p) = \frac{p+2W_\perp+6i\beta}{(p+W_\perp+6i\beta)^2+A_\parallel^2-W_\perp^2} + \frac{p+2W_\perp-3i\beta}{(p+W_\perp-3i\beta)^2+\frac{1}{4}A_\parallel^2-W_\perp^2} + \frac{p+2W_\perp-6i\beta}{(p+W_\perp-6i\beta)^2-W_\perp^2}\,. \tag{79}$$

This result is in agreement with Abragam's Eq. (64) [Ref. 8, Chap. X], when it is applied to three pairs of lines characterized by $\delta=\pm A_\parallel$, $\pm\frac{1}{2}A_\parallel$, and 0, and making the identification $p=i\omega$, $W_\perp=\Omega$.

In the slow relaxation limit ($W_\perp=0$), the spectrun consists of five Zeeman-type lines shifted by the quadrupole effect:

$$\tfrac{1}{2}F(p) = \frac{1}{p-6i\beta} + \frac{1}{p-i(3\beta-\frac{1}{2}A_\parallel)} + \frac{1}{p-i(3\beta+\frac{1}{2}A_\parallel)} + \frac{1}{p+i(6\beta+A_\parallel)} + \frac{1}{p+i(6\beta-A_\parallel)}\,. \tag{80}$$

D. Mössbauer spectrum in presence of external field

Let us now consider a single crystal with uniaxial symmetry around Oz and observe photons propagating along Oz. In the presence of an external field applied parallel to Oz ($\mathcal{H}_Z=\alpha S_z = g_\parallel \mu_B H_0 S_z$) and taking account of the relative intensities of the components of the γ radiation, it is found that the Mossbauer spectrum[13] given by (elmg quadrupole transition, $I_g=0$, $I=2$)

$$F(p)=\tfrac{5}{2}\,(C/D+C'/D')\,. \tag{81}$$

It should be noted that the same expression is also valid for an isotropic powder ($A_\parallel=A_\perp$, $W_\parallel=W_\perp$, $\beta=0$) submitted to an external field parallel to the propagation direction of the γ ray.

E. Remark

The preceding results have been derived under the assumption that the levels associated with Hamiltonian $\mathcal{H}_0$ are equally populated ($\mathcal{H}_0/k_BT \ll 1$). If the electronic Zeeman Hamiltonian $\mathcal{H}_Z$ happened to be much larger than the hyperfine structure $\mathcal{H}_{\mathrm{hf}}$, contrary to what we assumed for simplicity, it could happen that $\mathcal{H}_Z/k_BT \gtrsim 1$ while $\mathcal{H}_{\mathrm{hf}}/k_BT \ll 1$. But when $\mathcal{H}_Z \gg \mathcal{H}_{\mathrm{hf}}$ the hyperfine interaction may be reduced to its diagonal part and, as already mentioned, this simple case has been studied by a number of authors.

V. APPLICATION TO EXPERIMENTAL STUDY OF Yb*Au* ALLOYS

Dilute Yb*Au* alloys have already been the subject of numerous experiments[17-22] which have shown that the ytterbium is in a trivalent state whose lowest electronic state is the Kramers doublet Γ_7 separated by about 80 K from the next electronic levels Γ_6 and Γ_8.

Using the 84.3-keV Mössbauer transition of ^{170}Yb in dilute ^{170}Tm *Au* sources, we have studied the relaxation spectra of ytterbium in gold. Preliminary results have already been published.[23,24]

A. Sample preparation

The two metals (Au, purity 5*N*5 and Tm, purity 3*N*) were melted together in an induction furnace under argon atmosphere, in a beryllium oxide crucible. The thulium had been neutron activated before the alloy was prepared. The dilute alloy samples were rolled so as to reduce the γ-ray absorption by the gold matrix and were then annealed to eliminate defects introduced by rolling. A number of different thulium concentrations were used (1.3, 0.75, 0.5, and 0.2 at.%) so as to test the influence of interaction effects between impurities. An inactive sample was prepared with 0.75-at.% thulium so as to verify that the thulium was in solution, using crystalline parameter and resistivity measurements at 300 and 4.2 K. This sample was later irradiated and annealed and gave Mössbauer results similar to the other samples.

B. Experimental setup

The cryogenic apparatus used to cool simultaneously the source under study and the single line mobile absorber $\mathrm{YbB_6}$ enriched in ^{170}Yb is shown schematically in Fig. 2. The setup is unusual in that it uses horizontal movement transmitted to the absorber under vacuum by means of a short rod of thermally insulating material followed by a stirrup which passes around the source. The absorber is cooled to about 15 K by soft copper braids connected to the liquid-helium reservoir. The driver is also under vacuum in a container fixed on the side of the cryostat at the position of an external window. The source is introduced from the top of the cryostat in an aluminum jacket transparent to γ rays, and which can contain thermal exchange gas. Its temperature is controlled to ± 0.02 K near 1.3 K and to ± 0.05 K near 20 K. Among other advantages this system allows one to change the source rapidly without warming up the cryostat and without demounting the moving parts. In addition the transmission of the movement to the absorber takes place under better conditions than in the cryostats with vertical movements, which need much longer connection rods. The velocity was calibrated using a ^{57}Co source fixed at the opposite end of the drive. The cryostat has a capacity of 5 l of liquid helium, which allows runs up to three days. The

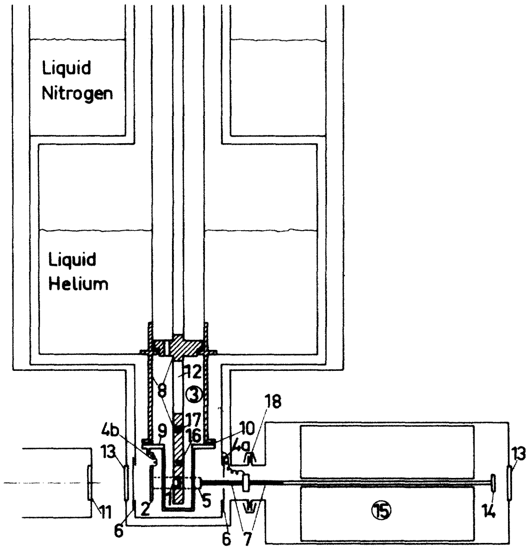

FIG. 2. Schematical representation of the experimental setup. 1: source; 2: mobile absorber; 3: thermal exchange chamber; 4: braided copper wires for thermalization (a) liquid-nitrogen temperature and (b) liquid-helium temperature; 5: stirrup transmitting the movement to the absorber (represented only by dotted lines); 6: aluminum foil shields; 7: Fiberglas rod; 8: copper parts; 9: aluminum jacket; 10; indium joint; 11: Ge(Li) detection diode; 12: Tufnol rod; 13: beryllium windows; 14: Co^{57} source for calibration; 15: drive under vacuum; 16: thermometer (germanium resistance); 17: heating resistance; 18: rubber O ring.

γ rays were detected using a Ge(Li) diode which was needed to separate the 84.3-keV γ ray of ^{170}Yb from the x rays at 69 and 78.6 keV produced by the decay of ^{170}Tm in gold.

C. Results and discussion

Figure 3 compares Mössbauer spectra obtained between 1.3 and 20 K with the sample having the lowest concentration in thulium (0.2 at.%) with the best least-square-fit curves using the theoretical formulas for the isotropic case in the absence of magnetic field. In addition to the spin flip rate W, the isomer shift, the intensity of the spectrum, and the background level were fitted by the use of a computer. On the other hand, the hyperfine constant A of the excited state of ^{170}Yb was taken as $A/h = 910$ MHz, using the value deduced from EPR measurements[22] carried out on ^{171}Yb, and the Mössbauer linewidth was fixed at the value of $\Gamma_{\text{expt}} = 2.7$ mm/s obtained with the same absorber and a source of TmB_{12}[23] which is close to the natural linewidth.

The small deviations between the theoretical line shape and the experimental one for slow-relaxation spectra, which we have already mentioned,[3] are least when the thulium impurity concentration is lowest and appear to be due to inhomogeneities in the crystal field due to neighbor effects. Much more dilute alloys are being studied.

The behavior of the spin-flip rate W as a function of T is shown in Fig. 4. The linear law expected at low temperatures according to the Korringa-type relation[3]

$$W = \frac{1}{2T_1} = \frac{2\pi}{\hbar} g^2 \left(\frac{g_J - 1}{g_J}\right)^2 [J_{sf}\, n(E_F)]^2 k_B T \quad (82)$$

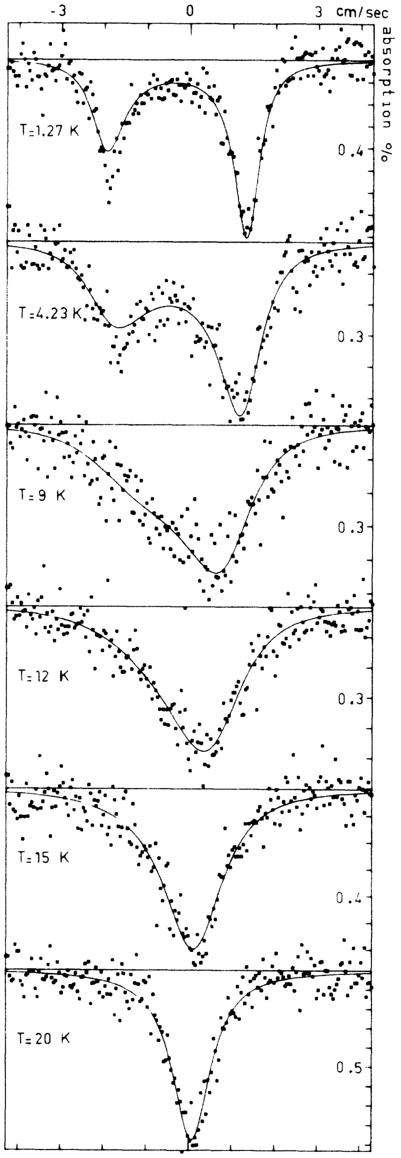

FIG. 3. Experimental spectra of Yb^{170} in gold. The solid line represents the result of a least-square fitting (see text). In our representation the positive velocities correspond to positive energies.

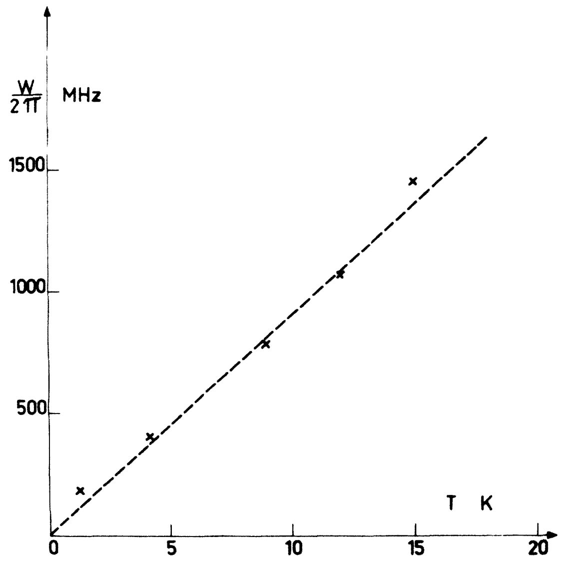

FIG. 4. Thermal evolution of the spin-flip rate. The dotted line represents the preliminary result given in Ref. 3.

is approximately obeyed and its slope gives an estimation of the coupling constant J_{sf} between the local moment and the conduction electrons:

$$|J_{sf}| = 0.38 \pm 0.03 \text{ eV} , \quad (83)$$

with $g = 3.43$ for Γ_7, $g_J = \frac{8}{7}$, and $n(E_F) = 0.16$ eV^{-1} per atom per spin. This value is in agreement with that obtained from EPR measurements [22]:

$$J_{sf} = -0.43 \pm 0.10 \text{ eV} . \quad (84)$$

A more detailed study is underway, the results of which will be published separately. Already it has been observed that at low temperatures the Korringa law is only approximately followed because of a Kondo anomaly which is exhibited by the relaxation rate.[24] This complements the recent resistance measurements of Murani[25] which also show Kondo behavior in Yb*Au* alloys.[26]

D. Remark

At temperatures below 1 K we are well into the slow-relaxation region; the line shape of the Mössbauer spectrum does not change appreciably any longer and ceases to give any precise information on the electronic relaxation rate. But when temperature becomes comparable to the hyperfine interval $\Delta = \frac{5}{2}A$, the ratio of the intensities of the two Mössbauer lines tend to depart from its high-temperature value $\frac{2}{3}$, due to unequal populations of the hyperfine sublevels. The extent to which thermal equilibrium is approached before Mössbauer emission depends on the ratio τ_n/T_1, where τ_n is the lifetime of the Mössbauer state. If τ_n/T_1 happens to be of order unity when $\Delta/k_B \gtrsim 1$, then the ratio of the intensities of the two Mössbauer lines gives complementary information on the electronic relaxation in this temperature range.

This problem, as well as that of the behavior of the electronic relaxation rate (and of the Kondo correction to it) when $\Delta/k_B T \gtrsim 1$, is investigated in more detail in a separate publication.[27]

VI. CONCLUSION

In conclusion we would like to emphasize the interest of the Mössbauer technique, together with the present theoretical interpretations, for the determination of electronic relaxation rates.

The other method most similar to the Mössbauer effect for such measurements is EPR. Nevertheless these two methods present certain differences which make them complementary.

On technical grounds, it has already been pointed out by Hirst[2] that the Mössbauer effect has the advantages of a larger temperature range, an easier temperature regulation, and is not affected by the metallic state of the samples. However, there also exist some differences of principle: EPR requires an applied magnetic field (which will be a source of trouble in the study of Kondo anomalies), Mössbauer effect does not. In EPR local symmetry defects mainly give rise to an additive (inhomogeneous) line broadening, while their effect in Mössbauer spectroscopy is to alter the general form of the spectrum.[24]

As concerns EPR the sum of both effects results in a linewidth of the form

$$\Delta H = a(c, H) + bT$$

(impurity concentration c, applied magnetic field H), where the intrinsic relaxation rate if represented by the second term bT. The residual linewidth $a(c, H)$ is often rather large, resulting in a reduced accuracy in the determination of T_1.

Conversely it should be noted that the Mössbauer technique cannot be so widely applied as EPR. Also the determination of T_1 is most precise when $1/T_1 \sim \Delta/\hbar$ (hyperfine interval); this last condition will not always correspond to the temperature range where the Kondo effect manifests itself.

ACKNOWLEDGMENT

We wish to thank Dr. F. Varret for useful discussions and for his help in fitting the spectra.

---

*This work is part of a Thèse de Doctorat d'Etat to be submitted to the University Paris Sud by F. Gonzalez-Jimenez (Registration CNRS n° A. O. 9345).

†On leave from the Universidad Central de Venezuela, Caracas.

‡Associé au Centre National de la Recherche Scientifique

(CNRS).

[1] M. J. Clauser and M. Blume, Phys. Rev. B 3, 583 (1971).

[2] L. L. Hirst, J. Phys. Chem. Solids 31, 655 (1970).

[3] F. Gonzalez-Jimenez and P. Imbert, Solid State Commun. 11, 861 (1972).

[4] A few formulas concerning Mössbauer relaxation spectra in the presence of external field are given in Sec. IV D.

[5] H. Gabriel, J. Bosse, and K. Rander, Phys. Status Solidi 27, 301 (1968).

[6] F. Hartmann-Boutron and D. Spanjaard, J. Phys. (Paris) 33, 285 (1972). In Eq. (31) of this reference the integral over t''' should read $\int_{t0}^{t''} dt'''$.

[7] The lattice density matrix ρ which comes into play in Eqs. (19) and (20) has been omitted in Eqs. (2) and (3) of Hirst's paper Ref. 2. This results in an inadequate handling of the lattice correlation functions and it follows that Eq. (4) of Hirst is not quite correct at low temperatures. In this equation, the following substitutions should be made: $J_q(\omega_{dc}, T) \to J_{-q}(\omega_{cd}, T)$; $J_q(\omega_{ab}, T) \to J_q(\omega_{ba}, T)$; and $J_q(\omega_{bc}, T) \to J_{-q}(\omega_{bc}, T)$.

[8] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., Oxford, England, 1961).

[9] As pointed out by H. Gabriel [Phys. Lett. A 32, 202 (1970)] another condition is that $\tau_c < \tau_n$, where τ_n is the lifetime of the excited nuclear state. But $1/\tau_n < \mathcal{H}_0/\hbar$ when the structure of the Mössbauer spectrum is observable: It follows that this condition is always fulfilled.

[10] E. Bradford and W. Marshall, Proc. Phys. Soc. Lond. 87, 731 (1966); L. M. Levinson and M. Luban, Phys. Rev. 172, 268 (1968).

[11] D. Spanjaard and F. Hartmann-Boutron, (a) J. Phys. (Paris) 30, 975 (1969); (b) J. Phys. (Paris) 33, 565 (1972).

[12] In the opposite case of low temperatures, τ_c being temperature independent for the large thermal baths of interest to us, the ω_a dependence of $J_q(\omega_a, T)$ is due to populations effects brought about by performing the thermal averages over the bath variables [case of Korringa relaxation at very low temperatures [Ref. 11(b)].

[13] W. Happer, Ann. Phys. (N. Y.) 48, 579 (1968).

[14] For an application see F. Hartmann and F. Hartmann-Boutron, Phys. Rev. A 2, 1885 (1970). More elaborate formulations can be found in textbooks on collision broadening in gases.

[15] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, N. J., 1957).

[16] In the case $S = \frac{1}{2}$ there is no intrinsic atomic quadrupole effect (such as is observed in free atoms). This is also true for level Γ_7 of Yb^{3+} in Au.

[17] P. E. Rider, K. A. Gschneidner, Jr., and O. D. McMasters, Trans. Metall. Soc. AIME 233, 1488 (1965).

[18] A. P. Murani, J. Phys. C Suppl. Metal Phys. 2, S153 (1970).

[19] L. L. Hirst, Gwyn Williams, D. Griffiths, and B. R. Coles, J. Appl. Phys. 39, 844 (1968).

[20] Gwyn Williams and L. L. Hirst, Phys. Rev. 185, 407 (1969).

[21] Gwyn Williams, Solid State Commun. 7, 1593 (1969).

[22] L. J. Tao, D. Davidov, R. Orbach, and E. P. Chock, Phys. Rev. B 4, 5 (1971).

[23] F. Gonzalez-Jimenez, P. Imbert, J. C. Achard, and A. Percheron Phys. Status Solidi A 19, 201 (1973).

[24] F. Gonzalez-Jimenez and P. Imbert, Solid State Commun. 13, 85 (1973).

[25] A. P. Murani, Solid State Commun. 12, 295 (1973).

[26] Let us recall that, since J_{sf} is in reality a function of $\vec{q}$, the inverse electronic relaxation time $1/T_1$, the Kondo correction to $1/T_1$, and the resistivity do not indeed measure the same averages over $J(\vec{q})$. See D. Davidov, K. Maki, R. Orbach, C. Rettori, and E. P. Chock, Solid State Commun. 12, 621 (1973).

[27] F. Gonzalez-Jimenez, F. Hartmann-Boutron, and P. Imbert (unpublished).