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# APPLICATION OF HIRST'S THEORY TO PHONON RELAXATION ; MÖSSBAUER LINESHAPE IN THE PRESENCE OF RELAXATION BETWEEN TWO ELECTRONIC KRAMERS DOUBLETS

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**Résumé.** — Nous examinons dans quelles conditions la théorie de relaxation de Hirst peut être appliquée de manière simple aux processus de relaxation par les phonons (hypothèse du *spectre blanc*, symétrie locale élevée). Nous étudions ensuite l'influence, sur la forme de raie Mössbauer, des processus de relaxation du type Orbach, qui mettent en jeu des niveaux intermédiaires réels.

**Abstract.** — We investigate the conditions under which Hirst's relaxation theory can be applied in a simple way to phonon relaxation processes (*white spectrum approximation*, high local symmetry). We then study the influence, on the Mössbauer lineshape, of the Orbach type relaxation processes, which involve real intermediate states.

## 1. Application of Hirst's theory to phonon relaxation.

— Hirst's relaxation theory has met with great success in the interpretation of the Mössbauer relaxation spectra of paramagnetic impurities in metals [1, 2]. The simplest case is that of an isolated electronic level with an effective electronic spin  $S$  and a hyperfine structure  $AI.S$ , the relaxation of  $S$  being due to its coupling  $-2J\alpha S.s$  with the conduction electrons. Except at very low temperatures, this interaction satisfies the *white spectrum* approximation, and in addition it is isotropic. This leads to a simple situation of *spherical relaxation*. In that case, it is found that the whole super-relaxation matrix which controls the Mössbauer spectrum can be expressed as a function of a single parameter  $T_{1S}$ , the relaxation time of the *bare* electronic spin (without hyperfine structure).

In *ionic crystals* paramagnetic relaxation is due to phonons. The longitudinal relaxation processes for a *bare* electronic doublet split by an external magnetic field (EPR situation) are summarized in ref. [3], eq. (10.66) (non Kramers ions) and eq. (10.68) (Kramers ions). There are several possible processes, direct ones, indirect ones involving virtual intermediate states (Raman processes), and indirect ones involving real intermediates states (Orbach processes). In addition the coupling hamiltonians corresponding to these processes are generally not well known. For these reasons it appears necessary to restrict the use of Hirst's theory to cases with high local symmetry (cubic or uniaxial) and to processes which satisfy the *white spectrum* approximation : by this we mean that the Fourier transforms  $J(\omega)$  of the lattice correlation functions, which come into play in the relaxation

calculations, must not depend on  $\omega$  for values of  $\omega$  less than or comparable with the hyperfine coupling constant  $A/\hbar$ . This condition excludes : for non-Kramers ions the direct process, and for Kramers ions both the direct and the first order Raman processes (which could be induced by the hyperfine interactions).

When these conditions are realized, the relaxation supermatrix of the atom with nuclear spin is simply related to the relaxation supermatrix of the atom without nuclear spin (see for example eq. (34) of [2]). It remains to reduce the number of parameters which enter that last matrix by making use of symmetry considerations. However, in the case of Kramers doublets where there is an arbitrariness in the choice of the basis states, this requires some care, for reasons which are discussed in reference [3], p. 650-656. Notice that the symmetry considerations which follow are valid whatever the origin of the relaxation (phonons, conduction electrons, ...).

**2. Symmetry considerations.** — **2.1 ISOLATED DOUBLET.** — As an example, let us consider a rare-earth ion with total angular momentum  $J$ , in a cubic field where its lowest electronic state is a Kramers doublet, and assume that we can consider only relaxation inside this doublet (no Orbach process). Let  $Ox$ ,  $Oy$ ,  $Oz$  be the fourfold cubic axes. We choose the basis functions  $|a\rangle$  and  $|a'\rangle$  of the Kramers doublet in such a way that :

$$\langle a | J_z | a' \rangle = 0, \quad \langle a | J_z | a \rangle = - \langle a' | J_z | a' \rangle.$$

With respect to this basis the matrix elements of  $J$  between  $|a\rangle$  and  $|a'\rangle$  are isomorphous to those of a spin  $S = \frac{1}{2}$  with respect to the eigenstates  $|+\frac{1}{2}\rangle$  and  $|-\frac{1}{2}\rangle$  of  $S_z$ .

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If we now consider the density matrix  $\sigma$  of the Kramers doublet, we also have an isomorphism between  $\sigma$  and the average value of  $S$  :

$$\sigma_{aa} + \sigma_{a'a'} = 1 ; \quad \sigma_{aa} - \sigma_{a'a'} = 2 \langle S_z \rangle$$

$$\sigma_{aa'} = \langle S_+ \rangle ; \quad \sigma_{a'a} = \langle S_- \rangle .$$

On the other hand, the general relaxation equations of the average value of a spin  $S = \frac{1}{2}$  have the form :

$$\frac{d}{dt} \langle S_x \rangle = D \langle S_x \rangle + E \langle S_y \rangle + F \langle S_z \rangle$$

$$\frac{d}{dt} \langle S_y \rangle = D' \langle S_x \rangle + E' \langle S_y \rangle + F' \langle S_z \rangle$$

$$\frac{d}{dt} \langle S_z \rangle = D'' \langle S_x \rangle + E'' \langle S_y \rangle + F'' \langle S_z \rangle .$$

(1)

Since  $\langle S \rangle$  is an average value, it is a physical observable. Its relaxation equations must therefore be compatible with the symmetry of its neighbourhood. In particular, in a cubic symmetry they must be invariant under the reversal of any of the fourfold axis and under interchange of two axes. For this, one must have :

$$E = F = D' = F' = D'' = E'' = 0$$

and

$$D = E' = F'' .$$

The relaxation supermatrix then depends only on one parameter  $F''$  which is equal to  $-1/T_{1S}$  where  $T_{1S}$  is the longitudinal relaxation time which could be measured in an EPR experiment.

Similarly, in the case of uniaxial symmetry the relaxation supermatrix will depend only on two parameters,  $F''$  and  $D = E'$ .

These results are in agreement with eq. (69) of reference [2]. In that reference eq. (69) was established by expanding the equation of evolution of the density matrix up to second order in the relaxation hamiltonian  $\mathcal{H}_1$ . The present demonstration shows that it is indeed valid whatever the order of the relaxation process. In particular, it gives an additional justification to the use of a corrected  $T_{1S}$  in the presence of Kondo effect in YbAu, at temperatures large compared with the hyperfine interval [4]. It also shows that it is possible to use eq. (69) of [2] for the interpretation of relaxation spectra involving high order relaxation processes by phonons (for example the second order Raman process). However, these results do not apply to processes involving real intermediate states, such as the Orbach processes. These will be considered in the next § 3.

**2.2 SYMMETRY CONSIDERATIONS FOR COUPLED ELECTRONIC DOUBLETS.** — Let us now consider (in cubic or uniaxial symmetry) the case of two Kramers doublets A and C with substates  $|a\rangle$ ,  $|a'\rangle$  and  $|c\rangle$ ,  $|c'\rangle$  defined in the same way as above, and assume that these states are coupled with one another

by relaxation processes. We may define a global density matrix for the two doublets, which will have matrix elements of the type  $\sigma_{aa}$ ,  $\sigma_{cc}$ ,  $\sigma_{aa'}$ ,  $\sigma_{cc'}$ ,  $\sigma_{ac}$ ,  $\sigma_{ac'}$  and so on. By analogy with the above considerations, it seems clear that there will be no coupling by relaxation processes between the diagonal matrix elements  $\sigma_{aa}$ ,  $\sigma_{a'a'}$ ,  $\sigma_{cc}$ ,  $\sigma_{c'c'}$  (which have the same transformation properties as  $\langle J_z \rangle$ ) and the low frequency off diagonal matrix elements  $\sigma_{aa'}$ ,  $\sigma_{a'a}$ ,  $\sigma_{cc'}$ ,  $\sigma_{c'c}$  (which have the same transformation properties as  $\langle J_x \rangle$ ,  $\langle J_y \rangle$ ). We shall make use of this result below.

**3. Mössbauer lineshape in the presence of electronic relaxation between two Kramers doublets.** — When the electronic ground state A of the Mössbauer ion is connected with an excited electronic state C by a real process (*Orbach process*), even if C is only slightly populated, this excited state should be included in the calculation of the Mössbauer spectrum.

In order to investigate the effect of this inclusion on the Mössbauer lineshape, we have done a prototype calculation for a trivalent  $^{170}\text{Yb}$  source ( $I = 2$ ,  $I_g = 0$ ). In this source, the Mössbauer level (with lifetime  $\tau_n = 1/\Gamma$ ) is fed by a Beta transition. If we assume for simplicity that electronic rearrangement after the Beta transition is very fast and that thermal equilibrium between A and C is reached before the emission of the  $\gamma$ -ray [5], the lineshape is given by ([2] eq. (5), [6]) :

$$I(\omega) \propto \text{Re} \left| \sigma_A \sum_{\substack{u=a,a' \\ v=a,a',c,c'}} \langle uo, um | \mathcal{U}(p) | vo, vm \rangle \right|$$

$$+ \text{Re} \left| \sigma_C \sum_{\substack{u=c,c' \\ v=a,a',c,c'}} \langle uo, um | \mathcal{U}(p) | vo, vm \rangle \right|$$

(2)

where  $\sigma_A$  and  $\sigma_C$  are the relative populations ( $\sigma_A + \sigma_C = 1$ ) of the two electronic levels (at temperatures where Orbach process is important, there is no nuclear orientation) ;  $p = \Gamma/2 - i\omega$  ;  $m$  is the eigenvalue of  $I_z$ . Finally,  $\mathcal{U}(p)$  is the Laplace transform of the evolution operator in the Liouville representation [2] :

$$\mathcal{U}(p) \equiv [\mathcal{V}(p)]^{-1} = \left[ p - \frac{i}{\hbar} \mathcal{H}_{\text{hf}}^x - \frac{i}{\hbar} \mathcal{H}_{\text{el}}^x - R \right]^{-1} \quad (3)$$

with :  $\mathcal{H}_{\text{hf}}$  = hyperfine hamiltonian ;  $\mathcal{H}_{\text{el}}$  = electronic hamiltonian (which defines the energies of the Kramers doublets),  $R$  = electronic relaxation matrix [6]. For the case of interest here, the Liouville matrix  $\mathcal{V}(p)$  is  $80 \times 80$ . In order to factorize it, we have assumed that  $\text{Yb}^{3+}$  occupies a site with uniaxial symmetry around  $Oz$ , and that it has a completely anisotropic hyperfine structure in both electronic states :

$$\mathcal{H}_{\text{hf}} = A_{\parallel}^{\text{A,C}} I_z S_z^{\text{A,C}} + \beta^{\text{A,C}} [3 I_z^2 - I(I+1)] \quad (4)$$

( $S_z^{\text{A,C}}$  = effective spin of A or C) The matrix of  $\mathcal{V}(p)$  then reduces to five  $16 \times 16$  matrices corresponding to the different eigenvalues  $m$  of  $I_z$ . Each of these has the form of figure 1.

	AA	CC	AC	CA
AA				
CC				
AC				
CA				

FIG. 1.

We must now specify the relaxation matrix  $R$ . As an example, we shall assume here that the relaxation between the two Kramers doublets A and C is due to phonons. Then one has transition probabilities [3]:

$$W_{u \in A \rightarrow v \in C} = W\uparrow \text{ and } W_{v \in C \rightarrow u \in A} = W\downarrow, \\ \text{with } W\downarrow/W\uparrow = \exp[(E_C - E_A)/k_B T] \doteq \sigma_A/\sigma_C.$$

Typically, the energy difference  $|E_A - E_C|$  between C and A is of the order of  $50 \text{ cm}^{-1}$ , corresponding to  $(E_B - E_A)/\hbar \sim 10^{13} \text{ rad/s}$ . On the other hand, values of  $W\uparrow$  around 20 K are of the order of  $10^{10} \text{ s}^{-1}$ , leading to  $W\downarrow \sim 3 \times 10^{11} \text{ s}^{-1}$ . Since  $W\uparrow, W\downarrow \ll (E_C - E_A)/\hbar$ , we can apply the *secular approximation* and decouple the evolutions of (AA, CC) from those of (AC, CA). It is then sufficient to consider the upper left quarter of the matrix in figure 8, that is an  $8 \times 8$  matrix. Finally, in this last matrix, we may, by virtue of the symmetry considerations of § 3 decouple the evolutions of the diagonal matrix elements  $aa, a' a', cc, c' c'$  from those of the off-diagonal elements  $aa', a' a, cc', c' c$ . There remains a  $4 \times 4$  matrix represented in figure 2.

In this matrix,  $\lambda_m = +\beta^A(3m^2 - I(I+1))$ ;  $K_m = +\beta^C(3m^2 - I(I+1))$ ;  $\omega_m = +A_{\parallel}^A m$ ;  $\theta_m = +A_{\parallel}^C m$ ;  $W\uparrow, W\downarrow$  have been defined above;  $W_d$  corresponds to the direct process inside A (that inside C is negligible compared with  $W\downarrow$ ). The standard electronic relaxation time inside A, as measured in an E. P. R. experiment would be:  $(1/T_{1s})_A = 2W_d + 2W\downarrow$ .

After inversion of the  $4 \times 4$  matrix of figure 2, one finds that the final expression  $I(p)/2$  for the lineshape is the real part of:

$$\sigma_A \sum_m \left[ 1 + \frac{2f_m(p)}{W\downarrow} \right] \times \\ \times \frac{[p + i\lambda_m + 2W\uparrow + 2W_d]}{[p + i\lambda_m + 2W\uparrow + W_d - f_m(p)]^2 + \omega_m^2/4 - [W_d + f_m(p)]^2} \\ + \sigma_C \sum_m \frac{[p + iK_m + 2W\downarrow]}{[p + iK_m + 2W\downarrow - g_m(p)]^2 + \theta_m^2/4 - [g_m(p)]^2} \quad (5)$$

with

$$f_m(p) = 2W\uparrow W\downarrow \frac{[p + iK_m + 2W\downarrow]}{[p + iK_m + 2W\downarrow]^2 + \theta_m^2/4}; \\ g_m(p) = 2W\uparrow W\downarrow \frac{[p + i\lambda_m + 2W_d + 2W\uparrow]}{[p + i\lambda_m + W_d + 2W\uparrow]^2 + \omega_m^2/4 - W_d^2}.$$

Notice that in the first line of eq. (5), the term in  $f_m(p)/W\downarrow$  in the first bracket arises from cross-effects of A and C. It is possible to check that the corresponding contribution to  $I(p)$  is indeed symmetric with respect to A and C.

Comparison of eq. (5) with eq. (79) of [2] shows that Orbach relaxation has two main effects: 1) the Mössbauer spectrum is the superposition of two spectra corresponding to A and C, 2) for each of these spectra the existence of the other electronic level gives rise to corrective terms involving  $W\uparrow$  and  $W\downarrow$ . Due to the presence among these terms of the fractions  $f_m(p)$  and  $g_m(p)$ , this correction does not result in a mere alteration of  $W_{\perp}$  in eq. (79) of [2], but creates a distortion of the lineshape. Only when  $\sigma_A \gg \sigma_C$  and when  $W\downarrow \gg p$ ,  $K_m, \theta_m$ , are the results of [2] restored. Then  $f_m(p) \simeq W\uparrow$ ;  $f_m(p)/W\downarrow \simeq \sigma_C/\sigma_A \ll 1$  and:

$$\frac{I(p)}{2} = \\ = \text{Re} \sum_m \frac{[p + i\lambda_m + (1/T_{1s})_A]}{[p + i\lambda_m + (1/2 T_{1s})_A]^2 + \omega_m^2/4 - [(1/2 T_{1s})_A]^2} \quad (6)$$

One should also notice that for the state A the correction associated with the quadrupole effect in the state C is of first order in  $(K_m/W\downarrow)$ , while that associated with the magnetic coupling is of second order in  $(\theta_m/W\downarrow)$ . This clearly arises from the fact that in the case of phonon relaxation, starting from one electronic substate of the Kramers doublet A, one has equal pro-

	aa	a' a'	cc	c' c'
aa	$p + i(\omega_m/2) + i\lambda_m + 2W\uparrow + W_d$	$-W_d$	$-W\uparrow$	$-W\uparrow$
a' a'	$-W_d$	$p - i(\omega_m/2) + i\lambda_m + 2W\uparrow + W_d$	$-W\uparrow$	$-W\uparrow$
cc	$-W\downarrow$	$-W\downarrow$	$p + i(\theta_m/2) + iK_m + 2W\downarrow$	0
c' c'	$-W\downarrow$	$-W\downarrow$	0	$p - i(\theta_m/2) + iK_m + 2W\downarrow$

FIG. 2.

bability of going to either of the substates of the Kramers doublet C, which have the same quadrupole effect, but opposite magnetic couplings.

An interesting particular case arises when  $\sigma_C \ll \sigma_A$  and at the same time  $K_m \gg \lambda_m$  (E. F. G. in C much larger than in A), so that we must keep terms of order  $K_m/W \downarrow$  in the spectrum of A. If we define  $\bar{\lambda}_m = \sigma_A \lambda_m + \sigma_C K_m$ , then the first line of eq. (5) becomes :

$$\frac{I'(p)}{2} = \text{Re} (\sigma_A^2 + 2 \sigma_A \sigma_C) \times \sum_m \frac{p + i\lambda_m + (1/T_{1S})_A}{[p + i\lambda_m + (1/T_{1S})_A] [p + i\bar{\lambda}_m] + \sigma_A \omega_m^2/4} \quad (7)$$

In the fast relaxation limit  $((1/T_{1S})_A \gg \lambda_m, \omega_m)$  it reduces to :

$$\frac{I'(p)}{2} = \text{Re} (\sigma_A + \sigma_A \sigma_C) \times \sum_m \frac{(1/T_{1S})_A}{(1/T_{1S})_A (p + i\bar{\lambda}_m) + \sigma_A \omega_m^2/4} \quad (8)$$

i. e. the spectrum is approximately the same as if the quadrupole coupling of A were replaced by the average quadrupole coupling of A and C. Such a situation is encountered in Yb-Ethylsulfate around 20-30 K (Borely, Gonzalez-Jimenez, Imbert, Varret, private communication).

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