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Mössbauer absorption and emission experiments in $\text{CaF}_2(^{57}\text{Fe})$: relaxation and after-effect study

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Résumé. — La totalité du spectre d'absorption Mössbauer d'impuretés de ^{57}Fe dans CaF_2 et la plus grande partie du spectre Mössbauer émis par une source de ^{57}Co dans CaF_2 (échantillon en poudre) proviennent d'ions Fe^{2+} substitués en site cubique. Une faible contribution provenant de l'état de charge Fe^{1+} ($3d^7$) est également détectée dans les spectres d'émission, mais on n'y observe pas de contribution de type Fe^{3+} . Le spectre émis par les ions Fe^{2+} en site cubique comporte à basse température deux contributions issues de niveaux électroniques excités, à long temps de vie, et peuplés hors équilibre thermique. La première de celles-ci émane du triplet de spin-orbit $^5\text{E}-\Gamma_4$ de faible énergie ($E \approx 16 \text{ cm}^{-1}$), dont les propriétés de relaxation ont été analysées d'autre part en spectrométrie d'absorption. La seconde émane probablement du niveau excité $^5\text{T}_2 - \Gamma_{5g}$ de grande énergie ($E \approx 5\,000 \text{ cm}^{-1}$).

Abstract. — The entire Mössbauer absorption spectrum of ^{57}Fe impurities in CaF_2 and the main part of the emission spectrum of a CaF_2 (^{57}Co) powder sample originate from substitutional Fe^{2+} ions in cubic sites. A weak Fe^{1+} ($3d^7$) charge state contribution is also detected in the emission spectra, but no Fe^{3+} contribution is observed. Two long-lived excited electronic level contributions are evidenced out of the thermal equilibrium in the low temperature emission spectra of the cubic site Fe^{2+} ions. The first originates from the low energy spin-orbit triplet $^5\text{E} - \Gamma_4$ ($E \approx 16 \text{ cm}^{-1}$), whose relaxation properties are also analysed by absorption spectroscopy, and the second probably originates from the highly excited level $^5\text{T}_2 - \Gamma_{5g}$ ($E \approx 5\,000 \text{ cm}^{-1}$).

1. Introduction.

Mössbauer emission spectroscopy (MES) studies in insulating or semi-conducting matrices often reveal atomic states which differ from those observed by Mössbauer absorption spectroscopy (MAS) in the corresponding host compound. These « abnormal » states may concern the charge, spin, energy, chemical bonding or local environment of the Mössbauer ion [1]. When these states present a transient character, the comparison of their life time θ with the life time τ_n of the Mössbauer nuclear state may provide useful information about the nature of the relaxation process towards equilibrium.

The interpretation of MES experiments in insulators or semi-conductors is generally hampered by a number of difficulties. Different after-effects may come into play together, giving intricate emission

spectra. Moreover, trivial physico-chemical effects related to the use of tracers may be easily confused with after-effects : for example, prior to the decay, part of the radioactive tracer may be located in unsuspected impurity phases, or inside abnormal surroundings on the surface of the sample or near crystalline defects within the bulk. Unambiguous characterization of transient states in MES experiments often requires additional investigations in order to well characterize the temporal behaviour of the observed species. Complementary technics are : electronic relaxation studies by MAS in the same matrix ; time differential Mössbauer emission spectroscopy (TDMES) ; optical excitation studies etc...

Here we give a full account of a comparative MAS and MES study of ^{57}Fe impurities in CaF_2 . Some results have been briefly reported elsewhere [2].

Fluorite (CaF_2) is a simple and convenient host-lattice, as it is a cubic, diamagnetic and highly ionic compound, where 3d impurities such as Fe^{2+} or Co^{2+} ions easily substitute on the cubic eightfold coordinated cation sites. The energy level scheme (Fig. 1) of the substitutional Fe^{2+} ions is of the same type as in the fourfold coordinated sites in the cubic ZnS matrix, where we have already performed a similar double MAS-MES study [3, 4]. Two interesting differences however exist between these two matrices. First, CaF_2 is an insulator whereas ZnS is a semi-conductor, and the different electrical behaviour may change the stability of the abnormal charge states following the decay of the ^{57}Co radioactive parent. Besides, the dynamical Jahn-Teller coupling [5], which modifies the electronic properties of the Fe^{2+} ions in ZnS, does not seem to play any significant role for Fe^{2+} in CaF_2 [6].

Chapter 2 describes the MAS experiments performed on a $\text{CaF}_2(^{57}\text{Fe})$ single crystal sample. The slowing down of the relaxation rates within the two lowest spin-orbit levels of the cubic site Fe^{2+} ions modifies the absorption lineshape at low temperature. This in turn allows the variation of the relevant relaxation rates to be measured.

Chapter 3 describes MES experiments performed on $\text{CaF}_2(^{57}\text{Co})$ powder and single crystal samples and chapter 4 analyses the relaxation lineshape of the Fe^{2+} ions in the emission spectra. The largest proportion of cubic site Fe^{2+} ions is observed in the powder source sample, where they contribute about 3/4 of the total emission area at room temperature. The remaining part of the spectrum essentially comes from Fe^{2+} ions in non cubic sites which are due to superficial impurity phases. A small additional line is assigned to monovalent Fe^{1+} ions in CaF_2 . The most important result of this MES study is the demonstration that two excited electronic levels of the substitutional cubic site Fe^{2+} ions contribute, out of the thermal equilibrium, to the low temperature emission spectra. The coherence of this interpretation is examined with respect to the MAS relaxation measurements on Fe^{2+} in CaF_2 (case of the $^5\text{E} - \Gamma_4$ level) and with respect to optical excitation measurements on Fe^{2+} in other cubic matrices (case of the $^5\text{T}_2 - \Gamma_{5g}$ level).

Chapter 5 contains a general discussion concerning the charge states, local symmetries and energy levels observed by MES in $\text{CaF}_2(^{57}\text{Co})$, and a comparison with other emission data, particularly those previously obtained in the ZnS (^{57}Co) sources.

2. Mössbauer absorption study on $\text{CaF}_2(^{57}\text{Fe})$.

2.1. OUTLINE OF PREVIOUS STUDIES. — An initial study of a ^{57}Fe doped CaF_2 single crystal, performed in 1976 by Régnard and Chappert [7], showed that near 9 K the absorption spectrum of the cubic site

Fig. 1. — Energy level scheme of the fourfold or eightfold coordinated Fe^{2+} ion ($3d^6, ^5D$) in cubic symmetry, from reference [16]. Left side levels: crystal field orbital splitting; middle and right side levels: spin-orbit levels calculated respectively within the first order and the second order spin-orbit and spin-spin interactions. Degeneracy numbers are given in brackets. Right side numbers are the relative values of the quadrupole interaction (QS) in each sublevel in the presence of strains (see Ch. 4).

Fe^{2+} ions was separated into two distinct contributions: a central line due to the Fe^{2+} ground state singlet $^5\text{E} - \Gamma_1$, and, in accordance with Ham's predictions [5], a low intensity quadrupole doublet due to the first excited triplet $^5\text{E} - \Gamma_4$ (Fig. 1). At higher temperature, the quadrupole doublet collapses due to relaxation averaging, whereas at lower temperatures its intensity vanishes because this level is no longer thermally populated. In a later MAS and far-infrared absorption study [6], Régnard and Dürr estimated the value of the energy separation between the two lowest spin-orbit levels Γ_1 and Γ_4 of the Fe^{2+} ion in CaF_2 to be $\delta \approx 17 \text{ cm}^{-1}$, and the value of the cubic crystal field energy splitting between the ground orbital doublet ^5E and the excited orbital triplet $^5\text{T}_2$ to be $\Delta \approx 5320 \text{ cm}^{-1}$. These authors also concluded that the dynamical Jahn-Teller coupling within the $\text{Fe}^{2+} ^5\text{E}$ state could be neglected to a first approximation. Soon after, we evaluated the electronic transition rates $W(\Gamma_4)$ within the triplet Γ_4 and $W(\Gamma_4 \rightarrow \Gamma_1)$ between the levels Γ_4 and Γ_1 in the temperature range

$10 \text{ K} \leq T \leq 27 \text{ K}$, by fitting the absorption spectra of reference [6] with a convenient relaxation lineshape [8]. We observed that below 15 K the electronic transition rate $W(\Gamma_4 \rightarrow \Gamma_1)$ became smaller than the nuclear decay rate $\Gamma = 1/\tau_n$ of ^{57}Fe (14.4 keV) and we predicted that the excited triplet Γ_4 should therefore remain populated out of the thermal equilibrium after the ^{57}Co decay in a MES experiment in CaF_2 below 15 K .

2.2. NEW STUDY IN THE RANGE $4.2 \text{ K} \leq T \leq 30 \text{ K}$. — As the expected phenomena in MES experiments actually occur at lower temperatures than we initially predicted ($T \approx 10 \text{ K}$ instead of $T \leq 15 \text{ K}$, see Ch. 3), we carried out a new MAS study using better experimental conditions, and we obtained relaxation results which are somewhat different from those of reference [8].

We used the same sample as in the previous studies of references [6, 7], namely a ^{57}Fe 400 ppm

at. doped CaF_2 single crystal. However this absorber was mounted differently. The crystal slice was glued with vacuum grease to an extra-pure aluminium disk instead of to a beryllium disk, and we used aluminized kapton foils instead of beryllium windows in the cryostat. Two different improvements were obtained in this way. First, the parasitic absorption spectrum due to iron impurities in the beryllium plates was eliminated. This provided a higher accuracy when measuring the weak absorption spectrum of this highly dilute $\text{CaF}_2(^{57}\text{Fe})$ sample (note that under the best observation conditions, i.e. near 8 K , the amplitude of the quadrupole doublet due to the Γ_4 level did not exceed 0.1% of the counting level). Secondly, the use of the aluminium disk holder, which is a much better heat conductor than the beryllium disk, eliminated a systematic error which affected the temperature measurements in the previous experiments. Five spectra chosen amongst the twelve recorded between 4.2 K and 30 K are represented in figure 2a. The spectra may be classi-

Fig. 2a. — $\text{CaF}_2(^{57}\text{Fe})$ low temperature absorption spectra. Fitted curves: see table I. The arrow marked quadrupole doublet, due to the $^5\text{E}-\Gamma_4$ excited level of the cubic site Fe^{2+} ions, vanishes below 8 K when this level is depopulated and above 10 K by relaxation averaging.

Fig. 2b. — $\text{CaF}_2(^{57}\text{Co})$ low temperature emission spectra (sample A). Fitted curves: see table II. Note that the arrow marked $^5\text{E}-\Gamma_4$ quadrupole doublet does not vanish below 8 K . Above 10 K the residual outer doublet is emitted by Fe^{2+} ions in non cubic sites.

fied into 2 categories according to their relaxation rates :

2.2.1 Slow relaxation spectra ($T \leq 8$ K). — The hyperfine characteristics of the slow relaxation contributions of the two lowest Fe^{2+} spin-orbit levels were fitted from the 4.2 K, 7 K and 8 K spectra (Table I). At these low temperatures, the ground singlet Γ_1 contributes a single line with a constant

linewidth whose isomer shift is :

$$IS(\Gamma_1) = 1.70 \pm 0.01 \text{ mm/s},$$

compared to a $\text{K}_4\text{Fe}(\text{CN})_6, 3 \text{ H}_2\text{O}$ reference absorber at 295 K. The first excited triplet Γ_4 contributes a quadrupole doublet whose isomer shift and separation values are respectively :

$$\begin{cases} IS(\Gamma_4) = 1.70 \pm 0.02 \text{ mm/s} \text{ (versus } \text{K}_4\text{Fe}(\text{CN})_6, 3 \text{ H}_2\text{O}) \\ QS(\Gamma_4) = 3.71 \pm 0.04 \text{ mm/s}. \end{cases}$$

We note that the isomer shift values $IS(\Gamma_1)$ and $IS(\Gamma_4)$ are the same to within the experimental errors. Moreover table I shows that the relative area values P of the quadrupole doublet, measured up to 10 K, agree with the relative Boltzmann population values $P_B(\Gamma_4)$ in the level Γ_4 , calculated using the relation :

$$P_B(\Gamma_4) = 3 \exp(-\delta/k_B T) [1 + 3 \exp(-\delta/k_B T)]^{-1} \quad (1)$$

and using for the Γ_4 level energy, the optically measured value $\delta = 15.8 \pm 0.2 \text{ cm}^{-1}$ [6].

As shown by Ham [5], the quadrupole splitting $QS(\Gamma_4)$ has the following origin : the triplet Γ_4 is split by random strains in the sample into three close diamagnetic singlets Γ_{4X} , Γ_{4Y} and Γ_{4Z} , which induce three equivalent axial electric field gradients (EFG) respectively along the OX , OY and OZ axes. As the sum of these three EFG is zero, no quadrupole interaction is observed in the Γ_4 level at the fast relaxation limit. But, at the slow relaxation limit, each of the three singlets contributes the same quadrupole doublet, whose theoretical separation value is [5] :

$$QS(\Gamma_4) = (6/7) q \langle r^{-3} \rangle_{3d} e^2 Q [I(2I - 1)]^{-1}. \quad (2)$$

In this expression, q is a reduction factor ($q \leq 1$) due to a possible dynamical Jahn-Teller effect. As already mentioned in reference [6], the experimental value of $QS(\Gamma_4)$ shows that here the q value is actually close to 1.

2.2.2. Intermediate relaxation spectra ($8 \text{ K} < T < 25 \text{ K}$). — Above 8 K, the quadrupole doublet broadens and then it collapses, so that the central line width goes through a maximum. The linewidth anomaly (Fig. 3a) is larger than in ZnS [3] and the

Table I. — $\text{CaF}_2(^{57}\text{Fe})$ absorber sample. Fitted data, using Lorentzian lineshapes (underlined values were imposed) : IS : isomer shift, relative to $\text{K}_4\text{Fe}(\text{CN})_6, 3 \text{ H}_2\text{O}$; G : full linewidth mid height; QS : quadrupole splitting; P : relative area; $P_B(\Gamma_4)$: calculated relative Boltzmann population of the 15.8 cm^{-1} energy level $^5E - \Gamma_4$.

N.B. At 15 K and 30 K, the quadrupole doublet due to the level $^5E - \Gamma_4$ is no longer resolved (relaxation averaging).

T (K)	central line			quadrupole doublet (level Γ_4)				
	IS (mm/s)	G (mm/s)	P (%)	IS (mm/s)	G (mm/s)	QS (mm/s)	P (%)	$P_B(\Gamma_4)$ (%)
30	1.70	0.37	100	—	—	—	—	—
15	1.70	0.79	100	—	—	—	—	—
10	1.70	0.36	77.5	<u>1.70</u>	0.72	3.40	22.5	23.6
8	1.70	0.31	84.1	<u>1.71</u>	0.45	3.71	15.9	14.9
7	1.70	0.31	88.2	1.70	0.42	3.71	11.8	10.4
4.2	1.70	0.29	98.7	<u>1.70</u>	<u>0.40</u>	<u>3.71</u>	1.3	1.3

Fig. 3. — Thermal variation of the central linewidth G . Open circle : fitted values, using a lorentzian lineshape. a : absorption experiments ; b : emission experiments (sample A). The dashed line curves represent the residual linewidth after subtraction of the same dynamical broadening part in both types of experiments. Full circles in figure 3b are fitted values of the static linewidth part in the emission relaxation spectra (see Ch. 4).

maximum value is observed here at a temperature twice as high (about 16 K instead of 8 K).

In order to analyse the relaxation phenomena in a quantitative way, we fitted the spectra using a stochastic relaxation lineshape adapted from the Tjon and Blume calculations [9], as already described in references [3, 8]. Within this model, the ^{57}Fe nucleus undergoes a randomly fluctuating EFG driven by two different relaxation mechanisms. First, the EFG reorients itself along the three crystalline directions OX , OY and OZ , as driven by the « elastic » transition rate $W(\Gamma_4)$ between the sublevels Γ_{4X} , Γ_{4Y} and Γ_{4Z} of the triplet Γ_4 . Secondly, the EFG can also take the value zero corresponding to the ground level Γ_1 . The occurrence of the latter value is governed by the « inelastic » transition rate $W(\Gamma_4 \rightarrow \Gamma_1)$ from any Γ_4 sublevel to the level Γ_1 , and by the reverse transition rate :

$$W(\Gamma_1 \rightarrow \Gamma_4) = W(\Gamma_4 \rightarrow \Gamma_1) \times \exp(-\delta/k_B T). \quad (3)$$

Energy levels above the Γ_4 level are neglected, as they are not appreciably populated in the considered temperature range. Several « static » parameters, such as isomer shift, quadrupole separation $QS(\Gamma_4)$ and limiting static linewidth, were fixed at

the values measured in the slow relaxation region, so that only two adjustable parameters were fitted in the intermediate relaxation region : the electronic transition rates $W(\Gamma_4)$ and $W(\Gamma_4 \rightarrow \Gamma_1)$. (N.B. These rates were respectively named W and W' in reference [8], and W'_4 and W_4 in reference [3]).

The fitted values are reliable only within a rather restricted temperature range :

$$10 \text{ K} \leq T \leq 21 \text{ K for } W(\Gamma_4)$$

and

$$8 \text{ K} \leq T \leq 16 \text{ K for } W(\Gamma_4 \rightarrow \Gamma_1). \quad (\text{Fig. 4})$$

Contrary to the case of $\text{ZnS}(^{57}\text{Fe})$, $W(\Gamma_4)$ cannot be neglected compared to $W(\Gamma_4 \rightarrow \Gamma_1)$ and both elastic and inelastic mechanisms are involved in the $\text{CaF}_2(^{57}\text{Fe})$ relaxation spectra. The two rates $W(\Gamma_4)$ and $W(\Gamma_4 \rightarrow \Gamma_1)$ have almost equivalent values at 10 K, but the thermal variation of $W(\Gamma_4)$ seems to be steeper than that of $W(\Gamma_4 \rightarrow \Gamma_1)$.

The most interesting result of this study is the fact that the electronic transition rate $W(\Gamma_4 \rightarrow \Gamma_1)$, which empties the excited level Γ_4 into the ground level Γ_1 , becomes smaller than the nuclear decay rate $\Gamma = 1/\tau_n = 7.09 \times 10^6 \text{ s}^{-1}$ of ^{57}Fe (14.4 keV) below the temperature $T \approx 9.8 \text{ K}$. This result is markedly different from the previous evaluation in the same sample [8], which estimated this temperature at $T \approx 15 \text{ K}$. As shown in the next chapter, the

Fig. 4. — Thermal variation of the electronic transition rates $W(\Gamma_4 \rightarrow \Gamma_1)$ (full circles and full line curve) and $W(\Gamma_4)$ (open circles and dashed line curve) in a Log-Log plot, from the absorption experiments. Note that $W(\Gamma_4 \rightarrow \Gamma_1)$ becomes smaller than the nuclear decay rate $\Gamma = 1/\tau_n$ below about 10 K.

new data is in agreement with the observation of a population out of the thermal equilibrium in the level Γ_4 in MES experiments below about 10 K.

As for the thermal variation curves of the relaxation rates $W(\Gamma_4)$ and $W(\Gamma_4 \rightarrow \Gamma_1)$, which are represented in a Log-Log plot in figure 4, they are respectively close to T^5 -type and T^4 -type temperature dependence. However the narrowness of the temperature range and the limited accuracy of the fits hinder unambiguous conclusions being derived about the exact nature of the phonon driven relaxation mechanisms from the above variations.

3. Mössbauer emission study on $\text{CaF}_2(^{57}\text{Co})$.

3.1. SAMPLE PREPARATION AND EXPERIMENTAL CONDITIONS. — It is worth briefly mentioning first some unsuccessful attempts to introduce ^{57}Co into the CaF_2 matrix. A first attempt consisted in wetting CaF_2 powder with a $^{57}\text{CoCl}_2$ solution in 0.1 N HCl, and then drying and annealing 15 h at 750 °C in a vacuum sealed silica tube. In a variant method, we tried to first obtain $^{57}\text{CoF}_2$ by adding a HF solution before the diffusion annealing. However the emission spectra did not contain any line attributable to Fe^{2+} in cubic sites. An X-ray diffraction on non radioactive check-samples then revealed the formation of Co_2SiO_4 during the annealing treatment in the silica tube. Although successful diffusion attempts were performed by annealing $\text{CaF}_2\text{-CoF}_2$ mixtures under argon atmosphere in a graphite crucible in an induction furnace, the latter method failed for low CoF_2 concentration levels, parasitic reactions occurring then on the cobalt.

Finally we succeeded in preparing the sources by annealing the CaF_2 samples with the $^{57}\text{CoCl}_2$ deposit under a dry HF gas flow. Three samples were prepared in this way :

Powder sample A. — High purity CaF_2 powder, wetted with $^{57}\text{CoCl}_2$ in HCl solution and then dried, was placed in a gold crucible inside a monel tube. After dehydration under HCl gas flow (2 h at 200 °C), both fluorination (2 h at 200 °C, then 2 h at 400 °C) and diffusion annealing (4 h at 700 °C) were performed under HF gas flow. The sample, of about 1 mCi activity, was kept under vacuum.

Single Crystal samples B_1 and B_2 . — Samples B_1 and B_2 were $\langle 100 \rangle$ oriented single crystal slices, respectively obtained by sawing and by cleaving a CaF_2 crystal. From these slices, two sources were prepared exactly in the same way as for the powder sample A.

The emission spectra were recorded using a moving single line $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ absorber containing 0.1 mg ^{57}Fe per cm^2 , whose linewidth, as observed with a reference source of ^{57}Co in rhodium, was $G_{\text{exp}} \approx 0.25$ mm/s.

3.2. STUDY OF THE $\text{CaF}_2(^{57}\text{Co})$ POWDER SAMPLE (A). — A detailed study of this sample was made : 21 emission spectra were recorded between 1.35 K and 573 K. The room-temperature spectrum is given in figure 5A and some representative low temperature spectra are given in figure 2b, where they are to be compared to the corresponding absorption spectra of figure 2a. Despite the complexity of these spectra, we obtained coherent fits by carefully following the thermal variation of the various components (Table II).

The room-temperature spectrum (Fig. 5A) contains three different contributions :

(a) A single line labelled Fe^{2+} (77 % relative area), whose linewidth ($G = 0.27$ mm/s) only slightly exceeds the minimum experimental width ($G_{\text{exp}} = 0.25$ mm/s). The isomer shift ($IS = 1.53 \pm 0.02$ mm/s, referred to $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) is the same as in the $\text{CaF}_2(^{57}\text{Fe})$ absorber [7]. This line is thus emitted by substitutional cubic site Fe^{2+} ions in CaF_2 .

(b) A very broad and indistinct doublet (not labelled in Fig. 5A), which however contains about 20 % relative area. Its large linewidth actually reveals the presence of a wide distribution of EGF values.

Fig. 5. — Room temperature (295 K) emission spectra of the various $\text{CaF}_2(^{57}\text{Co})$ samples. A : powder sample. B_1 : single crystal sawed slice. B_2 : single crystal cleaved slice. The diffusion process of ^{57}Co into CaF_2 is quite incomplete in the B_1 and B_2 samples (arrow marked Fe^{3+} and Fe^{2+} quadrupole doublets do not originate from the bulk). Fitted curves : see parameters in tables II (sample A) and III (samples B_1 and B_2).

Table II. — $\text{CaF}_2(^{57}\text{Co})$ powder sample (A). Fitted data, using Lorentzian lineshapes (abbreviations are listed in Table I. IS, G, QS are given in mm/s, P in %. Underlined values were imposed). Note that below 10 K the $^5\text{E} - \Gamma_4$ level of the cubic site Fe^{2+} ions contributes a quadrupole doublet, out of the thermal equilibrium.

N.B. This table contains only a sampling of the 21 fitted spectra of sample A.

T (K)	cubic site Fe^{2+} ions							non cubic site Fe^{2+}					Fe^+ ions		
	central line			doublet (level Γ_4)				n°	doublet (s)				single line		
	IS	G	P	IS	G	QS	P		IS	G	QS	P	IS	G	P
573	1.30	0.25	88	—	—	—	—	D	0.79	0.36	0.84	10	<u>1.80</u>	<u>0.30</u>	2
295	1.53 ± 0.02	0.27	77	—	—	—	—	D	1.22 ± 0.10	1.54	1.21 ± 0.10	20	2.06 ± 0.04	0.29	3
55	1.70 ± 0.02	0.44	61	—	—	—	—	D ₁	<u>1.40</u>	1.92	1.68 ± 0.20	32	2.30 ± 0.04	0.30	4
								D ₂	1.58 ± 0.04	0.29	3.25 ± 0.04	3			
30	1.70	0.64	60	—	—	—	—	D ₁	<u>1.40</u>	1.80	1.96	32	2.27	0.30	3
								D ₂	<u>1.60</u>	0.30	3.36	5			
15	1.69	1.08	61	—	—	—	—	D ₁	<u>1.40</u>	<u>1.60</u>	2.63	30	<u>2.27</u>	<u>0.30</u>	4
								D ₂	<u>1.60</u>	<u>0.30</u>	3.40	5			
10	1.70	0.90	53	<u>1.70</u>	0.71	3.61	9	D ₁	<u>1.40</u>	1.36	2.70	28	<u>2.27</u>	<u>0.30</u>	3
								D ₂	<u>1.60</u>	<u>0.30</u>	<u>3.40</u>	7			
8	1.71	0.92	50	1.70	0.48	3.72	17	D ₁	<u>1.40</u>	1.43	3.00	24	<u>2.27</u>	<u>0.52</u>	3
								D ₂	<u>1.60</u>	<u>0.30</u>	<u>3.40</u>	6			
4.2	1.69 ± 0.02	0.90	43	1.70 ± 0.02	0.36	3.75 ± 0.02	25	D ₁	1.40 ± 0.20	1.39	3.00 ± 0.20	24	<u>2.27</u>	0.52	2
								D ₂	<u>1.60</u>	<u>0.30</u>	<u>3.40</u>	6			

The isomer shift value ($IS = 1.22 \pm 0.10$ mm/s) as well as the thermal variation of the quadrupole separation (see below) are characteristic for Fe^{2+} ions, localized in non cubic sites.

(c) A small additional line labelled Fe^+ , visible on the right side of the main Fe^{2+} line. This weak and narrow line (relative area: 3 ± 1 %; linewidth $G = 0.29$ mm/s) presents a very large isomer shift: $IS = 2.06 \pm 0.04$ mm/s. From charge density calculations [10, 11], this isomer shift can only be attributed to $3d^7$ or $3d^8$ charge states. In fact, we assign this line to the $\text{Fe}^{1+} (3d^7)$ charge state, as in $\text{MgO} (^{57}\text{Co})$ [12] and other host compounds where very similar results were obtained (see Sect. 5.1).

The thermal evolution of the various components is the following :

(a) Contribution emitted by the cubic site Fe^{2+} ions :

Its thermal evolution, which is particularly interesting, presents two main steps :

i) From 573 K to about 15 K, this contribution can be fitted to a first approximation by a Lorentzian-shaped line with increasing linewidth, as in the MAS experiments. The linewidth variation curve (Fig. 3b) is particularly steep from 40 K to 15 K, due to the relaxation broadening, and its variation is then roughly parallel to that observed in MAS (Fig. 3a). The relaxation lineshape is actually the same in both MAS and MES experiments in this temperature range, because the condition $W(\Gamma_4 \rightarrow \Gamma_1) \gg 1/\tau_n$, for the thermal equilibrium to be achieved in the MES experiments within the Γ_1 , Γ_4 levels, is fulfilled for $T \geq 15$ K (see Fig. 4). However the MES linewidth is systematically larger than the corresponding MAS linewidth above 15 K (Figs. 3a and 3b). This extra line broadening probably comes from random strains which are larger in the source sample than in the absorber sample. This conclusion is supported by the fact that the linewidth difference between MES and MAS experiments slowly decreases as the temperature is raised.

ii) Below 15 K, one observes in figure 2b an increase of the intensity of the external Fe^{2+} doublet. As a matter of fact, the spectrum analysis (Table II) clearly demonstrates that this intensity increase does not concern the non cubic site doublets D_1 and D_2 , but another Fe^{2+} doublet, whose hyperfine characteristics are unambiguously those of the cubic site Γ_4 level contribution as observed in the MAS experiments. But, in contrast with the MAS results, the intensity of this contribution departs from the thermal equilibrium value. The intensity increase is particularly fast just below 10 K, as expected from the $W(\Gamma_4 \rightarrow \Gamma_1)$ transition rate measurements (Ch. 2). Below 4.2 K, where $W(\Gamma_4 \rightarrow \Gamma_1) \ll 1/\tau_n$, the area of the doubled becomes temperature independent and its saturation value is then about 37 % of the total area of the cubic site Fe^{2+} components. Another important feature of the low temperature emission spectra concerns the Fe^{2+} central line, whose linewidth remains abnormally large below 10 K (Fig. 3b) compared to the absorption linewidth at the same temperature (Fig. 3a). The origin of this line broadening is discussed later (Ch. 4).

(b) *Contribution emitted by non cubic site Fe^{2+} ions :*

The mean quadrupole separation and the linewidth of this broad-doublet increase with decreasing temperatures. Below about 60 K, the EFG distribution segregates towards two different values, so that two doublets are then required to account for this contribution : first, a very broad internal doublet (labelled D_1 , Table II) of 28 ± 4 % relative area, whose separation increases sharply from about 1.7 mm/s to a saturation value of 3.0 ± 0.2 mm/s below 10 K ; secondly, an external doublet with rather narrow linewidth, of 6 ± 2 % relative area, whose separation increases slowly from about 3.25 mm/s to a saturation value of 3.40 ± 0.04 mm/s below 30 K. This external doublet is visible, for example, in the spectra at 30 K and 15 K in figure 2b. It must be emphasized that the total area of the contribution (b), which represents 34 ± 4 % of the spectrum area below 77 K, decreases to about 20 % at 295 K and 10 % at 573 K. The apparent Debye temperature is thus much smaller for the non cubic Fe^{2+} components than for the substitutional

Fe^{2+} component, and for that reason we think that the contribution (b) is emitted by ^{57}Co atoms located in superficial phases. Further evidence of an incomplete diffusion process is observed in the single crystal spectra (see Sect. 3.3).

(c) *Contribution assigned to Fe^{1+} ions :*

This weak and narrow line remains observable up to the highest temperature (573 K) and its relative area does not seem to vary appreciably over the whole temperature range (Table II).

3.3. STUDY OF THE $\text{CaF}_2(^{57}\text{Co})$ SINGLE CRYSTAL SAMPLES B_1 AND B_2 . — The main part of the 295 K spectra of samples B_1 and B_2 (Fig. 5 and Table III) is made up of Fe^{2+} and Fe^{3+} quadrupole doublets, which we attribute to superficial layers of ^{57}Co rich phases as they strongly decrease after a surface cleaning of the slices. These doublets, which present some analogy with the $^{57}\text{CoF}_2$ spectrum observed by Friedt [13], probably belong to mixed calcium and cobalt fluorides. Such mixed superficial fluoride phases may also account for the non cubic Fe^{2+} component (b) with an abnormally low Debye-Waller factor, which is observed in the powder sample A (previous Sect.).

The relative area of the substitutional Fe^{2+} single line, which is 77 % in the powder sample A, is only 21 % in the sawed slice sample B_1 and 10 % in the cleaved slice sample B_2 , although the doping and annealing treatments were identical for the three samples. This shows that the more divided or uneven the surface, the more complete the ^{57}Co diffusion into the CaF_2 matrix. No detailed study of the cubic site Fe^{2+} fraction could be made in the crystal sources B_1 and B_2 , as the ^{57}Co substitutional fraction was too small in these samples.

4. Emission relaxation lineshape analysis. Probable contribution from the $^5\text{T}_2$ excited state.

In this chapter, we now examine in greater detail the emission lineshape of the cubic site Fe^{2+} fraction in the powder source sample A.

At the end of section 3.2 we already mentioned the different behaviour of the central linewidth in MES and MAS measurements below 10 K, that is in the slow relaxation region (Fig. 3).

Table III. — $\text{CaF}_2(^{57}\text{Co})$ single crystal samples. Fitted data, at $T = 295$ K. B_1 : sawed slice sample ; B_2 : cleaved slice sample (abbreviations are listed in Table I).

Sample	Fe^{2+} central line			Fe^{2+} quadrupole doublet				Fe^{3+} quadrupole doublet			
	IS (mm/s)	G (mm/s)	P (%)	IS (mm/s)	G (mm/s)	QS (mm/s)	P (%)	IS (mm/s)	G (mm/s)	QS (mm/s)	P (%)
B_1	1.58	0.62	21	1.46	0.42	2.63	60	0.50	0.46	0.54	19
B_2	1.58	0.82	10	1.45	0.40	2.64	73	0.50	0.34	0.48	17

In the MAS measurements below 10 K, the linewidth recovers the value it has above 40 K, that is on the other side of the relaxation anomaly, and the value at 4.2 K is only slightly larger than the room temperature value (Fig. 3a). This shows that the level of strain is particularly low in this absorber sample.

In the MES measurements on sample A (Fig. 3b), the width of the central line remains at a large value below 10 K: $G_0 \approx 0.88$ mm/s. We will see below that the strain-induced quadrupole interactions in the ground state level Γ_1 are not sufficient alone to account for this large value. An additional contribution to the central linewidth is in fact due to a second cubic Fe^{2+} metastable level, populated out of thermal equilibrium.

In order to follow the variation of both the strain-induced and the metastable contributions to the linewidth, we have to first subtract the dynamical line broadening due to fluctuations within the Γ_1 , Γ_4 levels. This dynamical broadening is given by the MAS linewidth anomaly ($10 \text{ K} \leq T \leq 40 \text{ K}$, Fig. 3a). Subtracting this dynamical broadening from the total MES linewidth leaves a residual linewidth represented by the dashed line curve in figure 3b. With increasing temperature, the residual linewidth decreases in two steps: a sharp decrease of about 0.3 mm/s between 10 K and 15 K, and a smooth decrease from about 20 K up to room temperature. As the thermal variation of the strain-induced quadrupole interaction is due to a progressive change in the spin-orbit level populations, the strain broadening can only account for the smooth variation of the curve. The sharp decrease could possibly imply that a local distortion takes place between 10 K and 15 K, but such an explanation is not realistic. We are going to show that one of the excited levels of the cubic site Fe^{2+} ion is responsible for the extra linewidth observed below 15 K.

To this aim, we applied to all the spin-orbit levels of the ^5E and $^5\text{T}_2$ states of the Fe^{2+} ion (Fig. 1) the analysis made by Ham [5] for the first excited level Γ_4 of ^5E . In other words, using the wave functions tabulated by Low and Weger [16], we evaluated the quadrupole interaction which should be observed in the various levels in the slow relaxation limit in the presence of a weak strain field. The corresponding QS values, listed on the right side of figure 1, are calculated neglecting any dynamical Jahn-Teller reduction factor, and they are given as relative values with respect to the value of $QS(\Gamma_4)$ as expressed in relation (2). We notice that the lowest level Γ_{5g} of the excited $^5\text{T}_2$ state yields a quadrupole separation which is one tenth of $QS(\Gamma_4)$, that is $QS(\Gamma_{5g}) \approx 0.37$ mm/s. In our opinion, part of the central line intensity originates from the $^5\text{T}_2-\Gamma_{5g}$ level, out of thermal equilibrium. This contribution, which probably already exists above 77 K, is present as a single line down to 15 K, but it splits between 15 K and 10 K when the relaxation rate within the

triplet $^5\text{T}_2-\Gamma_{5g}$ becomes slow enough. Due to its superimposition onto the single line contribution of the ground level Γ_1 , the small quadrupole splitting $QS(\Gamma_{5g})$ remains unresolved, but it enhances the total linewidth of the central line by an amount of about 0.3 mm/s, which is the value observed experimentally. Additional considerations support this hypothesis:

1) Optical excitation measurements made on Fe^{2+} in GaP [14] and InP [15] have shown that the non radiative life times of the $^5\text{T}_2-\Gamma_{5g}$ level are respectively 12 and 17 μs in these matrices at 4.2 K, whereas the radiative life time is about 15 μs . All these values are typically 100 times as long as the nuclear life time τ_n . Besides, the non radiative life time measured in InP is almost constant up to 77 K and it decreases rapidly at higher temperatures, due to $^5\text{T}_2 \rightarrow ^5\text{E}$ multiphonon relaxation. Under these conditions, despite the high energy of the $^5\text{T}_2-\Gamma_{5g}$ triplet (about 5000 cm^{-1}), this level may present a metastable character in MES experiments below some critical temperature which may be well above 77 K. In addition, it should be noted that the radiative transition $^5\text{T}_2 \rightarrow ^5\text{E}$, which is allowed for the fourfold coordinated Fe^{2+} ion in GaP and InP, is forbidden for the eightfold coordinated Fe^{2+} ion in CaF_2 which presents a local symmetry inversion centre.

2) In MgO, where the substitutional Fe^{2+} impurities occupy octahedral sites, the $^5\text{T}_2-\Gamma_{5g}$ level is now the ground level and it can be easily studied by MAS. Now such a study, made in 1968 by Leider and Pipkorn [17], showed that the corresponding absorption line just splits below 14 K, with a separation value $QS(\Gamma_{5g}) = 0.33$ mm/s.

3) Finally, the triplet $^5\text{T}_2-\Gamma_{5g}$ is the only Fe^{2+} level of the whole ^5D configuration level scheme, which presents such convenient properties concerning the QS value and the life time.

By fitting the low temperature emission spectra, we find that about one third of the central line intensity could originate from the split contribution of the $^5\text{T}_2-\Gamma_{5g}$ level.

Remark. — The above procedure which consists in subtracting the MAS dynamical line broadening from the total MES linewidth, in order to evaluate the strain-induced and the metastable contributions to the MES linewidth, implies that the MAS and MES relaxation lineshapes are taken to be identical. This is certainly true above 15 K where the condition $W(\Gamma_4 \rightarrow \Gamma_1) \gg 1/\tau_n$ is fulfilled, but this is only an approximation between 10 K and 15 K. A more rigorous evaluation was made by fitting the « static part » of the linewidth from the emission spectra, using a relaxation lineshape adapted to the emission spectroscopy (see Appendix) and using the dynamical parameters $W(\Gamma_4)$ and $W(\Gamma_4 \rightarrow \Gamma_1)$ from the

MAS results. In the latter procedure, the so-called « static » linewidth parameter includes all the linewidth contributions except the dynamical broadening due to the electronic relaxation in the Γ_1 , Γ_4 levels. The fitted values of this parameter (full circles, Fig. 3b) are actually in good agreement with the dashed line curve previously obtained using the subtraction procedure.

5. Discussion and conclusions.

In this chapter, we compare our MES results in $\text{CaF}_2(^{57}\text{Co})$ with the results of some other studies, and particularly with those previously obtained in $\text{ZnS}(^{57}\text{Co})$. We first examine charge state and local symmetry problems. Then, we consider the questions relative to the ionic energy levels which appear populated out of the thermal equilibrium in MES experiments.

5.1 CHARGE STATE AND LOCAL SYMMETRY. — An initial MES study of ^{57}Co in CaF_2 was performed in 1971 by Cruset and Friedt between 295 K and 77 K [18]. The spectra were fitted using 3 contributions : a) a cubic site Fe^{2+} single line, still considerably strain broadened at room temperature ; b) a quadrupole doublet with a smaller isomer shift, assigned to substitutional Fe^{2+} ions associated with a Ca^{2+} vacancy ; c) a Fe^{3+} quadrupole doublet ($\sim 19\%$ of the total area).

It is to be noticed that we did not observe any appreciable Fe^{3+} contribution in the powder sample A of $\text{CaF}_2(^{57}\text{Co})$, but that such a contribution is visible in the spectra of the single crystal samples B_1 and B_2 , where the ^{57}Co diffusion is much less complete. Thus, in our opinion, the Fe^{3+} charge state does not actually result from an after-effect inside bulk CaF_2 . When present, it more likely originates from superficial extra-phases (mixed Ca and Co fluoride layers?), which also probably contain the non cubic Fe^{2+} ions (see Sect. 3.3). In order to check this point, it would be interesting to prepare $\text{CaF}_2(^{57}\text{Co})$ sources by methods other than diffusion, for example by ^{57}Co implantation followed by a convenient annealing, and to examine whether non cubic Fe^{2+} , Fe^{3+} and components are again present or not. It is to be noted that we also did not observe the presence of a Fe^{3+} charge state in $\text{ZnS}(^{57}\text{Co})$ [3, 4], although Fe^{3+} ions are often thought to be systematically observed in insulators or in semi-conductors, following the Auger cascade after the ^{57}Co decay.

Concerning the $\text{Fe}^{1+}(3d^7)$ state, it is interesting to compare our results in $\text{CaF}_2(^{57}\text{Co})$ with data previously obtained in the sources $\text{ZnS}(^{57}\text{Co})$, $\text{MgO}(^{57}\text{Co})$ and $\text{CaO}(^{57}\text{Co})$ and in the absorber $\text{KMgF}_3(^{57}\text{Fe})$ after γ irradiation.

In $\text{ZnS}(^{57}\text{Co})$ [4], the thermal variations of the second order Doppler shift and of the Debye-Waller factor are the same for the Fe^{1+} and Fe^{2+} ions. The effective Debye temperature is thus found to be the same for both Fe^{1+} and Fe^{2+} in ZnS , and therefore the Fe^{1+} ions seem to belong to ZnS bulk. The abrupt disappearance of the Fe^{1+} single line at 255 K is attributed to the transient character of this ion in this semi-conducting matrix, with the Fe^{1+} life time becoming much smaller than the nuclear life time τ_n for $T > 255$ K. Both MES [4, 19] and optical excitation measurements [20] in ZnS show that the Fe^{1+} ions transform into Fe^{2+} ions by giving an electron to the conduction band, through a 0.2 eV energy activation process.

In MgO [12] and in CaO [21], the effective Debye temperature associated with the Fe^{1+} ion ($\theta_D \sim 150$ K) is found to be much lower than that of the Fe^{2+} ion ($\theta_D \sim 400$ K). The Fe^{1+} ions are then attributed to a surface state, in which hydroxyl groups probably replace oxygen ions in the lattice.

In CaF_2 , the effective Debye temperature seems to be roughly the same for Fe^{1+} and Fe^{2+} , which suggests that the Fe^{1+} ions are located in the bulk as in ZnS . But the transformation process of Fe^{1+} into Fe^{2+} by giving an electron to the conduction band is no longer possible in the insulating compound CaF_2 , which probably explains the persistence of the Fe^{1+} emission line up to high temperatures in contrast with the ZnS results.

The isomer shift difference between Fe^{1+} and Fe^{2+} in CaF_2 is practically temperature independent and its mean value is :

$$IS(\text{Fe}^{1+}) - IS(\text{Fe}^{2+}) = 0.56 \pm 0.04 \text{ mm/s}.$$

This value is identical to the value observed in $\text{KMgF}_3(^{57}\text{Fe})$ absorbers, where the metastable Fe^{1+} charge state was generated by γ irradiation [22]. A comparable value (0.55 mm/s) was also measured in $\text{MgO}(^{57}\text{Co})$ at 77 K [12]. It should be remarked that the isomer shift difference between the Fe^{1+} and Fe^{2+} lines in all these ionic compounds is about twice as large as the isomer shift difference predicted between pure $3d^7$ and $3d^6$ configurations in the Table of Walker, Wertheim and Jaccarino [10]. This discrepancy cannot simply result from the choice of the isomer shift calibration constant for ^{57}Fe , as the relative value

$$\frac{\Delta |\psi(0)|^2 (\text{Fe}^{2+} - \text{Fe}^{1+})}{\Delta |\psi(0)|^2 (\text{Fe}^{3+} - \text{Fe}^{2+})},$$

as measured in various ionic compounds, is also much larger than the theoretical value corresponding to free ion $3d^7$, $3d^6$ and $3d^5$ configurations. Possible origins of these discrepancies have been discussed in reference [21].

5.2 ELECTRONIC LEVELS POPULATED OUT OF THERMAL EQUILIBRIUM. — The observation of the Fe^{2+} , $^5\text{E}-\Gamma_4$ excited level contribution, below 10 K, in the $\text{CaF}_2(^{57}\text{Co})$ emission spectra is a new manifestation of the persistence of abnormal electronic populations in a Mössbauer ion, after the decay of its radioactive parent. In CaF_2 as in ZnS , where this effect was observed for the first time [3], the MAS measurements of the $W(\Gamma_4 \rightarrow \Gamma_1)$ transition rate enabled predictions to be made about the metastable character that the level Γ_4 should present in low temperature MES experiments, and they removed any ambiguity about the assignment of the corresponding quadrupole doublet in the emission spectra.

Let us recall that the second excited spin-orbit triplet Γ_5 of the ^5E state of the Fe^{2+} ion can also give a slow relaxation quadrupole doublet, whose separation $QS(\Gamma_5)$ is equal to $QS(\Gamma_4)$ when the dynamical Jahn-Teller effect is neglected (see Fig. 1). In the cubic ZnS matrix, where an appreciable Jahn-Teller coupling modifies differently the Γ_4 and Γ_5 electronic wave functions, $QS(\Gamma_5)$ is much smaller than $QS(\Gamma_4)$ and both quadrupole doublets were separately evidenced as metastable contributions in the low temperature emission spectra [3]. In CaF_2 , where the dynamical Jahn-Teller effect can be neglected, only one quadrupole doublet is evidenced and, on the basis of the relaxation measurements, it was assigned to the metastable contribution of the level Γ_4 . However it cannot be excluded that both levels $^5\text{E}-\Gamma_4$ and $^5\text{E}-\Gamma_5$ contribute to the total intensity of the same doublet below 10 K. This prevents the evaluation of the electronic transition rates $W(\Gamma_4 \rightarrow \Gamma_1)$ and $W(\Gamma_5 \rightarrow \Gamma_1)$ to be derived from the respective intensities of the $^5\text{E}-\Gamma_4$ and $^5\text{E}-\Gamma_5$ contributions, as in the case of $\text{ZnS}(^{57}\text{Co})$. Finally, let us mention that a tentative assignment of the low intensity doublet D_2 (Table II) to the $^5\text{E}-\Gamma_5$ level of the cubic site Fe^{2+} ions would not be realistic: this assignment would imply very different relaxation properties for the two closely related $^5\text{E}-\Gamma_4$ and $^5\text{E}-\Gamma_5$ levels (the doublet D_2 is resolved at least up to 55 K, whereas the doublet assigned to the level $^5\text{E}-\Gamma_4$ collapses at about 15 K); the isomer shift difference (0.10 ± 0.02 mm/s) between the $^5\text{E}-\Gamma_4$ and $^5\text{E}-\Gamma_5$ contributions would be also unexplained.

The assignment of a metastable contribution to the level $^5\text{T}_2-\Gamma_{5g}$ in the $\text{CaF}_2(^{57}\text{Co})$ emission spectra is much more indirect than for the $^5\text{E}-\Gamma_4$ level: no electronic relaxation information is available from MAS experiments and the corresponding quadrupole doublet only appears as a line broadening in the MES experiments. However this assignment, which results from a careful analysis of the

central emission linewidth, seems very plausible for the reasons developed in chapter 4. It is to be remarked that such a metastable contribution from the $^5\text{T}_2-\Gamma_{5g}$ level is also very likely present in the emission spectra of $\text{ZnS}(^{57}\text{Co})$ below 8 K: the figure 3 of reference [3] indeed shows very different MAS and MES linewidths in the slow relaxation region ($T < 8$ K), whereas the two linewidths are exactly the same at higher temperatures.

To conclude, we note that the energy level population anomalies observed here on the Fe^{2+} ion in CaF_2 contribute to the growing number of such cases known from MES studies, for example, in the electronic Zeeman levels of the Fe^{3+} ion in $\text{LiNbO}_3(^{57}\text{Co})$ [23] and in the hyperfine levels of the $^{170}\text{Yb}^{3+}$ ion diluted in Au [24] and Pd [25].

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Appendix.

We describe below the modification made to the relaxation lineshape analysis previously used to fit the absorption spectra of the Fe^{2+} ions in ZnS [3] and in CaF_2 (this paper, Ch. 2), in order to adapt this lineshape to the emission spectra (Ch. 4).

The general emission relaxation lineshape [26, 27] involves the evolution of the density matrix of the electro-nuclear system during the nuclear life time. The solution of the problem is much simplified, as in the case examined here, when the electronic and nuclear variables can be calculated separately and when the relaxation processes do not introduce off-diagonal terms in the electronic density matrix. Then, the relaxation lineshape can be adapted from the MAS to the MES by modifying the populations of the relevant electronic states [28].

The absorption relaxation lineshape, which derives from a stochastic model of Tjon and Blume [9], was described in reference [3]. It assumes that only the two first levels Γ_1 and Γ_4 of the cubic site Fe^{2+} ions are appreciably populated in the considered temperature range, and that the electronic transitions are governed by the intra-level transition rate $W(\Gamma_4)$ inside the triplet Γ_4 , and by the inter-level transition rates $W(\Gamma_4 \rightarrow \Gamma_1)$ and $W(\Gamma_1 \rightarrow \Gamma_4)$. The adaptation from MAS to MES simply consists in replacing the Boltzmann density matrix, which governs in MAS the relative populations in the Γ_1 , Γ_4 level multiplicity, by the density matrix built from the following population values:

$$— \text{singlet } \Gamma_1 : P(\Gamma_1) = 1 - P(\Gamma_4)$$

— triplet Γ_4 :

$$P(\Gamma_4) = \frac{P_0(\Gamma_4) + 3 E \tau_n W(\Gamma_4 \rightarrow \Gamma_1)}{1 + (1 + 3 E) \tau_n W(\Gamma_4 \rightarrow \Gamma_1)}, \quad (4)$$

with $E = \exp(-\delta/k_B T)$.

The expression (4) for $P(\Gamma_4)$ is derived from the relation (5.3) of reference [3]. At the fast relaxation limit ($\tau_n W(\Gamma_4 \rightarrow \Gamma_1) \gg 1$), $P(\Gamma_4)$ is equal to the Boltzmann value $P_B(\Gamma_4)$ given by relation (1). At the slow relaxation limit ($\tau_n W(\Gamma_4 \rightarrow \Gamma_1) \ll 1$), $P(\Gamma_4)$ is equal to $P_0(\Gamma_4)$, the initial population of the triplet Γ_4 immediately after the ^{57}Co decay. Practically, $P_0(\Gamma_4)$ is given by the limit value of $P(\Gamma_4)$ when

the temperature tends to zero, that is by the limit value of the area of the quadrupole doublet coming from the level Γ_4 , expressed as a fraction of the total area emitted by the cubic site Fe^{2+} ions. This value is : $P_0(\Gamma_4) = 0.37$ (see Sect. 3.2).

Remark. — The emission lineshape given above assumes that the $^5\text{E}-\Gamma_5$ level is not appreciably populated. This is certainly true in the intermediate relaxation temperature range (10 K-20 K) where this lineshape is used. However, as mentioned in section 5.2, part of the limiting low temperature quadrupole doublet intensity could originate from the $^5\text{E}-\Gamma_5$ level out of thermal equilibrium. In this case $P_0(\Gamma_4)$ would be smaller than 0.37. However this would not affect the conclusions drawn from the use of this relaxation lineshape in chapter 4.

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