Lamb–Mössbauer factor of electronically excited molecular states measured by time-differential Mössbauer emission spectroscopy

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The Lamb–Mössbauer Factor (LMF) of molecular crystals is expected to depend on the electronic molecular states by their different intramolecular vibrational frequencies. Revisiting Mössbauer spectra obtained by time differential Mössbauer emission spectroscopy of the low spin compound $[^{57}Co/Mn(bipy)_3](PF_6)_2$ (bipy $= 2, 2'$-bipyridine) a ratio of 1.25 for the LMFs of the low spin ground state and of an excited high spin state decaying in the Mössbauer time window could be evaluated. The difference found is in line with the change of LMF observed for spin crossover compounds where the excited high spin state is populated by the so-called LIESST effect. The initial population of the high spin state is close to 100%.

1.   Introduction

The contribution of intra molecular vibrational frequencies in molecular crystals to the Lamb–Mössbauer Factor (LMF) was studied in great detail in a spin crossover system [1]. The so-called LIESST effect (Light Induced Excited Spin State Trapping) provides the unique opportunity to study the difference of the LMFs of molecules in two different electronic spin states. At low temperatures the molecules are in the low spin state and can be excited by green light to the metastable high spin state. This way the LMF of the iron nucleus as the center of a large molecule in two different molecular electronic states can be measured at the same temperature. Since the iron atoms are highly diluted in an isomorphous crystal of another metal $M (= Co, Mn, Zn, \ldots)$ ion, and because the change of the electronic state at the iron center (high spin to low spin) has almost negligible influence on the bonding between the molecules, the observed decrease of the LMF is essentially due to the decrease of intra molecular vibrational frequencies accompanying the transition from low spin to the high spin state. The evaluation of the temperature dependence of the LMF in $[Fe_xZn_{1-x}(ptz)_6](BF_4)_2$ (ptz $=$ propyltetrazole, $x = 0.005$) between 4.2 K and 50 K (above 50 K the lifetime of the metastable high spin state is too short for Mössbauer measurements) yields a frequency ratio of $\Omega_{LS}/\Omega_{HS} = 1.24$ and high spin frequencies of $\Omega_{HS}^{T_{1u,b}} = 45$ cm^{-1} and $\Omega_{HS}^{T_{1u,s}} = 227$ cm^{-1} of the two active $T_{1u,b,s}$

modes in cubic symmetry which were taken as an approximation for the octahedrally coordinating monodentate ptz-ligands. With these frequencies the ratio f_{LS}/f_{HS} of the LMF is calculated over the whole temperature range up to 400 K. It increases from 1.02 at 4.2 K almost linearly to 1.25 at 400 K [1].

In Mössbauer emission spectroscopy of low spin compounds which are related to Fe^{2+} spin crossover compounds three subspectra of the nucleogenic iron are observed besides the Fe^{2+} low spin ground state. These are two high spin states of Fe^{2+} and an aliovalent Fe^{3+} low spin state. In the system $[^{57}Co/Mn(bipy)_3](PF_6)_2$ (bipy = 2,2′-bipyridine) one of the high spin states could be identified as the LIESST state by comparing the lifetimes obtained from Time Differential Mössbauer Emission Spectroscopy (TDMES) measurements and the excited state of the Fe doped compound after laser excitation [2]. In analogy to LIESST the population of the exited HS state by nuclear decay has been called NIESST (Nuclear Induced Excited Spin State Trapping) [3]. TDMES has been used to separate the information of initial population of the different states of the nucleogenic iron from the decay time of the excited states, only a combination of both being accessible with Time Integral Mössbauer Emission Spectroscopy (TIMES) measurements. TDMES measurements were so far always evaluated with the constrain of equal LMFs of all subspectra.

2.   Results and discussion

The time integral and time differential Mössbauer emission spectra at 83 K of $[^{57}Co/Mn(bipy)_3](PF_6)_2$ (70 μCi, 6 weeks measureing time) are shown in figure 1. The spectrometer is described in [4]. The fitted curve is calculated by the time filtering theory for thick absorbers ($t_{eff} = 4.5$).

The four subspectra are plotted in the time integral emission spectrum (top of figure 1). The parameters (isomer shift and quadrupole splitting) obtained from the time integral spectrum were fixed in fitting the time differential spectra. Also the distribution (of Lorentz type) of emission lines of natural widths fitted to the time integral spectra were used in fitting the TDME spectra. The time filtered spectra were calculated neglecting relaxation effects according to Lynch et al. [5]. The relative areas of the four species in each of the time windows are the free parameters for the time differential spectra. The time evolution of the areas A_{LS}, A_{HS_1}, A_{HS_2}, and $A_{Fe^{3+}}$ contain information about the initial populations $N_{0\alpha}$, the LMF f_α and the lifetime Θ_α ($\alpha = LS(Fe^{2+})$, $HS_1(Fe^{2+})$, $HS_2(Fe^{2+})$, Fe^{3+}) of the different states forming after the electron capture (EC) of the ^{57}Co and the following Auger cascade and recombination processes at the nucleogenic iron. The areas at each time t are proportional to the LMF and the number of decays of the actual number $N_\alpha(t)$ of nuclei in state α. The time spectra are evaluated using the assumption that the Fe^{3+} and HS_2 do not decay in the measured time window at 83 K and 103 K. Then there is only the lifetime of the HS_1 state ($\Theta = \Theta_{HS_1}$) involved and the population of the HS_1 and LS states is
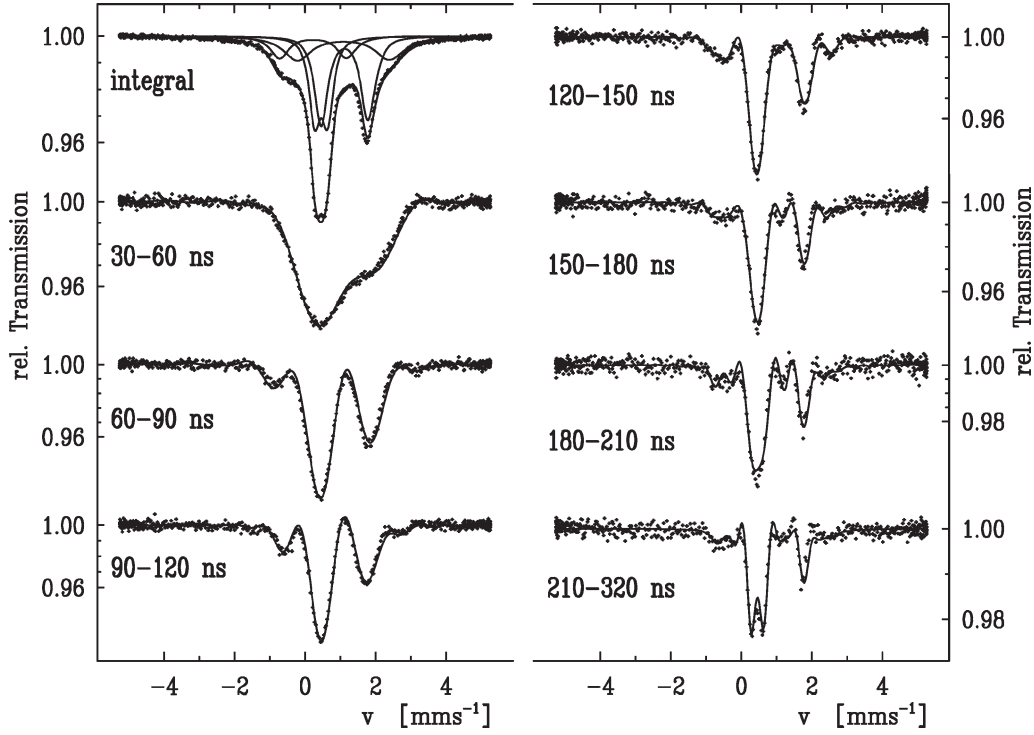
Figure 1. TIMES (top) and TDMES of $[^{57}\text{Co/Mn(bipy)}_3](\text{PF}_6)_2$ at 83 K, the solid lines are calculated according to the time filtering theory with parameters taken from the four subspectra shown in the time integral spectra.

given by

$$N_{\text{LS}}(\Theta, t) = N_{0\text{LS}} + N_{0\text{HS}_1} - N_{\text{HS}_1}(\Theta, t), \tag{1}$$

$$N_{\text{HS}_1}(\Theta, t) = N_{0\text{HS}_1} \exp(-t/\Theta), \tag{2}$$

where the decay of the HS_1 state to the LS state is single-exponential. The number of decays $N_{\text{HS}_1}(\Theta, t_a, t_e)$ in the time window $\{t_a, t_e\}$ after the detection of the preceding 122 keV γ quanta, which leads to the population of the 14.4 keV Mössbauer level at time T after the EC, is given by the double integral

$$N_{\text{HS}_1}(\Theta, t_a, t_e) = \int_0^\infty W(T)\, \text{d}T \int_{t_a}^{t_e} N_{\text{HS}_1}\big(\Theta, t' + T\big) w\big(t'\big)\, \text{d}t',$$

$$W(T) = \frac{1}{\tau_{122\,\text{keV}}} e^{-T/\tau_{122\,\text{keV}}}, \tag{3}$$

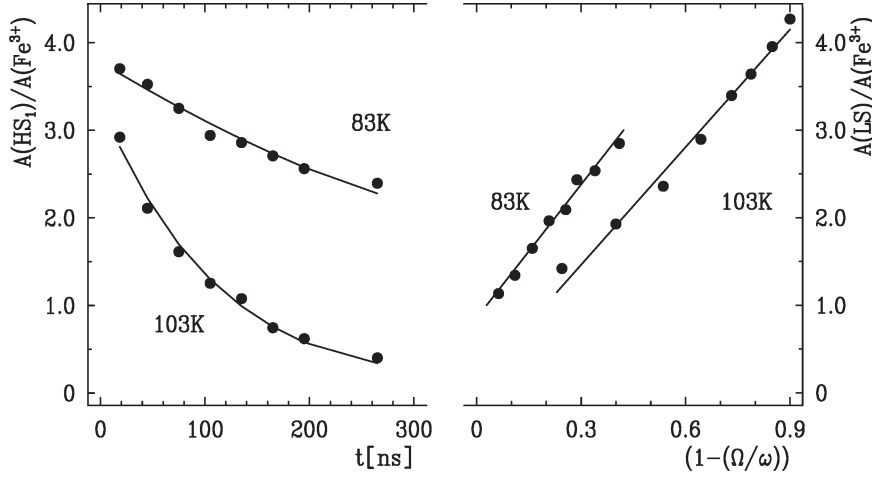$$w(t) = \frac{1}{\tau_{14.4\,\text{keV}}} e^{-t/\tau_{14.4\,\text{keV}}},$$

Figure 2. Area ratio of the HS_1 and Fe^{3+} doublets versus time t (left) and of the LS and Fe^{3+} doublets versus $(1 - \Omega/\omega)$ (right) at 83 K and 103 K.

where $W(T)$ and $w(t)$ are the probabilities at times T, t the nucleus being in the 122 keV and 14.4 keV states, respectively. The number of decays are expressed as $N_{HS_1}(\Theta, t_a, t_e) = N_{0HS_1}\Omega(\Theta, t_a, t_e)$, the function Ω being the integral of eq. (3). For infinite lifetime Θ the function Ω reduces to

$$\Omega(\infty, t_a, t_e) = \omega(t_a, t_e) = \exp(-t_a/\tau_{14.4}) - \exp(-t_e/\tau_{14.4}).$$

The area $A_{HS_1} \sim f_{HS_1}N_{HS_1}$ divided by the time independent area $A_{Fe^{3+}} \sim f_{Fe^{3+}}N_{Fe^{3+}}$ of the Fe^{3+} fraction gives the ratio $A_{HS_1}/A_{Fe^{3+}} = \gamma_1\Omega(\Theta, t_a, t_e)$ shown in figure 2 plotted versus the center of the time window $t = (t_a + t_e)/2$. The expression for γ_1 is given in eq. (4). The fits determine the lifetimes $\Theta(83\ \text{K}) = 507 \pm 43$ ns, $\Theta(103\ \text{K}) = 111 \pm 6$ ns of the HS_1 state and the factors $\gamma_1(83\ \text{K}) = 3.91 \pm 0.31$, $\gamma_1(103\ \text{K}) = 3.68 \pm 0.16$. With the known function $\Omega(\Theta, t_a, t_e)$ the corresponding area ratios of A_{LS} state and $A_{Fe^{3+}}$ are then plotted versus $(1 - \Omega(\Theta, t_a, t_e)/\omega(t_a, t_e))$. $A_{LS}/A_{Fe^{3+}} = \gamma_2 + \gamma_3(1 - \Omega/\omega)$ is a linear function of $(1 - \Omega/\omega)$ defining two further constants:

$$\gamma_1 = \frac{f_{HS_1}N_{0HS_1}}{f_{Fe^{3+}}N_{0Fe^{3+}}}, \qquad \gamma_2 = \frac{f_{LS}N_{0LS}}{f_{Fe^{3+}}N_{0Fe^{3+}}}, \qquad \gamma_3 = \frac{f_{LS}N_{0HS_1}}{f_{Fe^{3+}}N_{0Fe^{3+}}}. \qquad (4)$$

From ratios of the γ_j the Fe^{3+} properties drop out and the ratio of the LMFs $f_{LS}/f_{HS_1} = 1.30 \pm 0.13$, 1.25 ± 0.15 and the initial populations $N_{0LS}/N_{0HS_1} = 0.16 \pm 0.08$, 0.03 ± 0.12 at 83 K and 103 K are left, respectively. This result compares well with the LMF of the $^5T_{2g}$ LIESST state in the spin crossover compound $[Fe/Zn(ptz_6)](BF_4)_2$ which is extrapolated to be 10% lower than the LMF of the LS state at 100 K. The much higher ligand field energy of the $^5T_{2g}$ state in a LS compound is expected to be responsible for the larger differences as a result of weaker bonding. The initial population of the HS_1 state close to 100% has to be compared with the initial population observed in emission spectra of ^{57}Co doped in spin crossover compounds. These experiments [6]

show only the HS state with lifetimes much longer than the Mössbauer time window. The difference between a low spin compound and a spin crossover compound, the larger energy gap for the former one, does not obviously affect the initial population although it has dramatic effects on the lifetime of the HS state according to the inverse energy gap law of radiationless transitions [7].

Acknowledgement

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