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The lattice dynamics of the Fe(tpa) $(NCS)_2$ complex: light-induced excited spin state trapping effect

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A light-induced excited spin state trapping (LIESST) experiment for a thermal gradual spin crossover complex, Fetris (2-pyridylmethyl) amine$(NCS)_2$ or Fe(tpa) $(NCS)_2$, was attempted for the first time. The high spin (HS) state after light inducement stayed metastable over a period of days without relaxation at 10 K. Intersystem relaxation from a high to a low spin (LS) complex occurred at 50 K after bleaching at 10 K. Investigation of the Mössbauer spectra of the LIESST and relaxation experiment indicated that the Debye–Waller factor was a correlation parameter of the HS fraction and that the co-operative effect played a role in the relaxation process for such a solid compound.

1. Introduction

A new photophysical effect named light-induced excited spin state trapping (LIESST) in some thermal spin crossover complexes was found by Decurtins *et al.* [1, 2] ten years ago. This effect shows that for some spin crossover compounds, exhibiting thermal spin transitions, quantitative light-induced changes from LS $(^1A_1) \rightarrow HS(^5T_2)$ can be observed at quite a low temperature. Discovery of the LIESST effect has applications in fast optical switching devices and eventually for information storage [3]. "Spin equilibrium" of a compound may be disturbed greatly and relax to another "spin equilibrium" in various ways. It has been found that the relaxation behaviour follows first-order kinetics [4, 5] for many "spin equilibrium" systems in the solution. However, it is difficult to predict the relaxation behaviour of a solid system because of the contribution from the lattice effects. Recently, the LIESST effect has become a useful tool for the investigation of spin relaxation in a solid system [6].

The complex Fe(tpa) $(NCS)_2$, where tpa stands for tris(2-pyridylmethyl) amine, has been studied to show the gradual thermal spin transition [7, 8]. The first LIESST effect and relaxation experiment for the compound are shown in this paper.

2. Experimental procedure

The ligand tpa as well as the Fe(tpa)$(NCS)_2$ compound were prepared by the modification method [8]. Small yellow needles were obtained after several episodes of recrystallization in pyridine, and the purity of the needles was checked by hydrogen nuclear magnetic resonance (H-NMR), infrared (i.r.) spectroscopy and the melting point.

Mössbauer effect measurements were performed using a conventional constant acceleration spectrometer in the transmission mode with a $^{57}Co/Rh$ source (at room temperature). All isomer shifts are reported here with respect to the source. The Mössbauer spectra were analysed using the so-called transmission integral evaluation technique as well as a least-squares fitting procedure with Lorentzian lines in the MOSFUN program [9]. A thin ($3.66\ mg/cm^{-2}$ natural iron) powder sample of complex Fe(tpa) $(NCS)_2$ was sealed in a polished Plexiglas container and mounted in a helium-flow cryostat in order to allow the light to pass easily through the absorber.

LIESST experiments were carried out on a complex Fe(tpa)$(NCS)_2$ absorber at 10 K. Optical pumping was done by irradiating the sample under a 450 W Xe-arc lamp for 2 h. Some filters were used to cut out the green light during optical pumping. Relaxation of $HS(^5T_2) \rightarrow LS(^1A_1)$ occurred after warming the absorber to 50 K after LIESST experimentation at 10 K. The Mössbauer spectra were recorded every 2 h during the relaxation process.

3. Results and discussion

The Mössbauer spectra for complex Fe(tpa)$(NCS)_2$ before and after irradiation are shown in Fig. 1. Because the compound was very sensitive to moisture, some impure HS–Fe^{2+} (about 5%) with Mössbauer

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parameters of quadrupole splitting (QS) of 2.49 mm s^{-1} and an isomer shift (IS) of 1.21 mm s^{-1} at 10 K was found during the study [8] of the temperature dependent Mössbauer spectra and magnetic susceptibility measurement of the sample. Besides this impurity, the spectrum before irradiation indicates that some residual HS–Fe^{2+} phase (3% in total transition HS and LS phases) with (QS = 3.11 mm s^{-1} and IS = 0.97 mm s^{-1}) still coexists with the LS–Fe^{2+} phase (97%) (QS = 0.73 mm s^{-1} and IS = 0.31 mm s^{-1}). After irradiation for 2 h the light spectrum shows that more than the 90% LS–Fe^{2+}($^1A_1$) state converts into the HS–Fe^{2+}($^5T_2$) state at the same temperature. The metastable HS state remains so stable that no obvious HS → LS relaxation appears at 10 K over a period of days. Such a successful LIESST effect for a Fe(tpa)(NCS)$_2$ complex has not been reported before, as far as we know. Heating the sample up to 80 K causes the metastable HS state to relax back completely to the LS state in 30 min (this spectrum is also shown in Fig. 1).

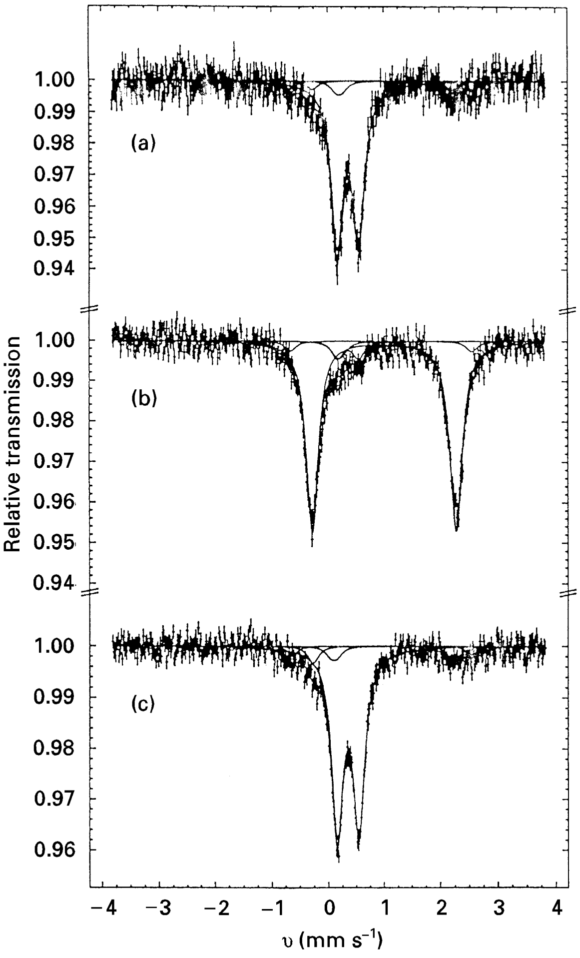

Figure 1 LIESST experiment with Fe(tpa)(NCS)$_2$: (a) before irradiation at 10 K, (b) after irradiation at 10 K, and (c) after heating to 80 K.

From quantitative analysis of the Mössbauer spectra (Table I), the hyperfine parameters of LS–Fe^{2+} and HS–Fe^{2+} were found to differ little during the LIESST experiment at 10 K. However, the Mössbauer effect of the spectrum (containing most of the LS state) before irradiation is obviously stronger than that of the spectrum (containing most of the HS state) after irradiation. Thereby the Debye–Waller factors of $f(10\,K) = 0.784$ before irradiation and $f(10\,K) = 0.836$ after irradiation are evaluated from the effective thicknesses of the spectra, respectively. The Debye–Waller factor in the main LS phase (HS fraction, $\gamma_{HS} = 0.04$) is about 6% larger than that in the main HS phase ($\gamma_{HS} = 0.93$) at 10 K.

In order to study the relaxation process of HS($^5T_2$) → LS($^1A_1$) the absorber was warmed to 50 K after optical pumping and the $^5T_2$ state was converted into the $^1A_1$ state slowly (in about 36 h) at this temperature. In Fig. 2 it is easy to observe that the relative intensity of HS decreases with increasing time, and that the metastable HS state disappears completely after about 2000 min. Furthermore, relaxation analysis of the Fe(tpa)(NCS)$_2$ Mössbauer spectra at 50 K indicates that the high spin fraction is strongly dependent on time (Fig. 3). It is found that the relaxation process takes almost 1800 min from $\gamma_{HS} = 0.8$ to 0.5, i.e. at a relatively slow rate. However, after $\gamma_{HS} < 0.5$ the HS fraction suddenly decreases to $\gamma_{HS} = 0.1$ in 240 min. The non-linear curve of $ln(1 - \gamma_{HS})$ versus time in Fig. 3 indicates that the complex does not follow first-order kinetics behaviour during the relaxation process. It may be thought that the co-operative forces of the lattice in this situation influence the manifestation of the spin relaxation in the solid compound. Moreover, it is difficult to explain such physical relaxation phenomenon because the Mössbauer spectra techniques available are somewhat more limited for such relaxation processes in the solid state [10]. However, the co-operation effect of the lattice may be evaluated from the Debye–Waller factors that are also affected by intermolecular interaction.

The Debye–Waller factors (Fig. 4) of the compound were calculated for each spectrum in the relaxation process and differed slightly from $f = 0.59 \pm 0.04$ at $\gamma_{HS} = 0.75 \pm 0.03$ to $f = 0.64$ at $\gamma_{HS} = 0.1$. This indicates that the lattice dynamics of the compound in a defined relaxation time period depend on the HS-fraction at 50 K. It is understood that the

TABLE I Parameters of Mössbauer spectra in LIESST experiment

Temperature T (K)	LS–Fe^{2+}				HS–Fe^{2+}				
	γ_{HS}	t^a	QS (mm s^{-1})	IS (mm s^{-1})	t	QS (mm s^{-1})	IS (mm s^{-1})	f	Θ_D(K)
Before irradiation 10	0.04	1.602	0.384	0.350	0.070	2.562	0.991	0.836	50.0
After irradiation 10	0.93	0.108	0.384	0.351	1.464	2.492	0.962	0.784	43.5
Warming to 80	0.05	1.024	0.388	0.346	0.082	2.514	0.980	0.548	47.2

t is the effective thickness. f is the Debye–Waller factor for the whole compound. Θ_D is the Debye temperature for the whole compound and is calculated by the Debye model at a low temperature limit (T = 10 K) and at a high temperature limit (T = 80 K), respectively.

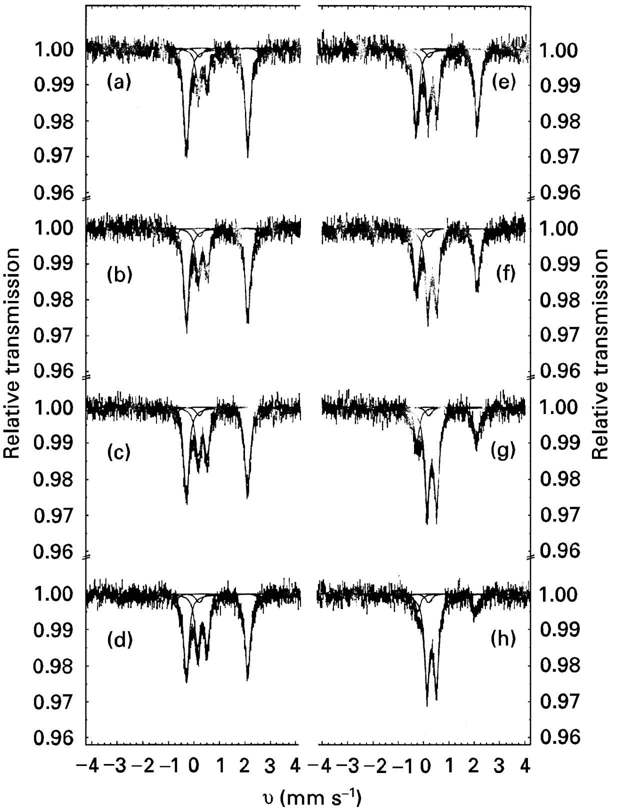

Figure 2 Mössbauer relaxation spectra of Fe(tpa)$(NCS)_2$ at 50 K as a function of time. After (a) 0 min, (b) 240 min, (c) 420 min, (d) 1320 min, (e) 1560 min, (f) 1800 min, (g) 1920 min, (h) 2040 min.

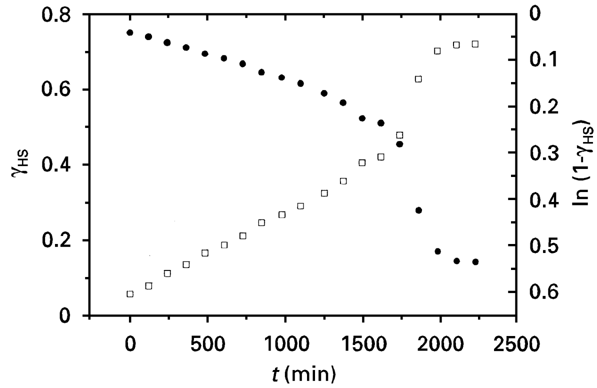

Figure 3 The HS fraction, γ_{HS} (●), and logarithm of $1 - \gamma_{HS}$ (□) as a function of relaxation time at 50 K.

Debye–Waller factor of the compound changes with the HS fraction because crystal lattice expansion follows the LS ⇒ HS transition, which in turn leads to a softening of the lattice and thus to a decrease of the Debye-temperature. In fact, the volume of the lattice decreases with decreasing HS-fraction in the spin transition because of the different unit cell volumes of the HS and LS molecules [11]. The contribution to the Debye–Waller factor in the compound is from intermolecular interaction between the spin sites and from intramolecular interaction in a certain spin molecule. The difference between the Debye–Waller factors in the low and high spin states from the contribution of the intramolecular has been estimated to be less than 3% from the temperature dependent measurements of magnetic susceptibility and Mössbauer spectra, whereby intramolecular interaction is the same for the HS and LS states during the Mössbauer timescale of 10^{-8} s. Therefore the greatest contribution to the different Debye–Waller factors in the HS and LS states is from intermolecular interaction during the relaxation process.

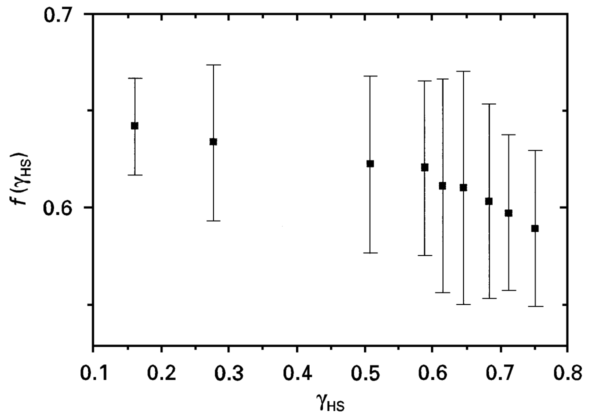

Figure 4 The Debye–Waller factor of the complex as a correlation parameter of HS fraction, γ_{HS}, at 50 K.

Direct evidence for the co-operative effect was determined from a diluted mixed spin transition crystal [12]. The change in the Debye temperature of the lattice and the intermolecular co-operative effect depend on the dilute per cent of metal ions. The dilute complexes $[Zn_{1-x}Fe_x(ptz)_6]$ $[BF_4]_2$, while the dilute complex x is < 0.1, do not influence the Debye–Waller factor derived from the intermolecular interaction contribution and do not give rise to a co-operative effect in the crystals [12].

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