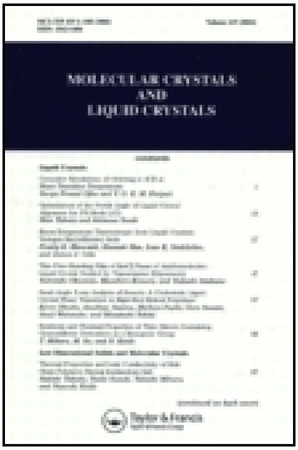

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Intersystem Crossing and Light-Induced Bistability in Iron(?) Spin-Crossover Compounds

Andreas Hauser [a] , Jelena Jefti [a] , Harald Romstedt [a] & Roland Hinek [b]

[a] Institut für anorganische und physikalische Chemie, Universität Bern, Freiestrasse 3, CH-3000, Bern, 9, Switzerland

[b] Institut für Anorganische Chemie und Analytische Chemie, Johannes-Gutenberg-Universität Mainz, Staudingerweg 9, D-55099, Mainz, Germany

Version of record first published: 04 Oct 2006.

To cite this article: Andreas Hauser , Jelena Jefti , Harald Romstedt & Roland Hinek (1996): Intersystem Crossing and Light-Induced Bistability in Iron(?) Spin-Crossover Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 286:1, 217-224

To link to this article: http://dx.doi.org/10.1080/10587259608042289

Mol. Cryst. Liq. Cryst., 1996, Vol. 286, pp. 217–224
Reprints available directly from the publisher
Photocopying permitted by license only

INTERSYSTEM CROSSING AND LIGHT-INDUCED BISTABILITY IN IRON(II) SPIN-CROSSOVER COMPOUNDS

ANDREAS HAUSER*, JELENA JEFTIĆ, HARALD ROMSTEDT
Institut für anorganische und physikalische Chemie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

ROLAND HINEK
Institut für Anorganische Chemie und Analytische Chemie, Johannes-Gutenberg-Universität Mainz, Staudingerweg 9, D-55099 Mainz, Germany

Abstract The dynamics of the high-spin→low-spin intersystem crossing process in iron(II) spin-crossover compounds are strongly influenced by cooperative effects of elastic origin which are due to the large difference in volume between high-spin and low-spin complexes. The deviation from first order kinetics is attributed to a build-up of an internal pressure as the relaxation proceeds, leading to a characteristic self-acceleration. The elastic interactions may lead to a light-induced bistability for systems which otherwise remain in the high-spin state down to cryogenic temperatures.

INTRODUCTION

So-called spin-crossover compounds of transition metal ions with a d^5 to d^7 electron configuration, that is compounds exhibiting an entropy driven transition from a low-spin (LS) state a low temperatures to a high-spin (HS) state at elevated temperatures have been known for several decades, and their properties have been periodically reviewed .[1] By far the largest number of spin-crossover compounds is known for iron(II) with six d-electrons. Because of the large difference in metal-ligand bond length Δr_{HL} between the $^5T_2$ (HS) and the $^1A_1$ (LS) state of ~0.2 Å,[2] and the concomitant difference in volume ΔV_{HL},[3] interactions of elastic origin between spin changing molecules lead to cooperative phenomena in concentrated materials. These manifest themselves in thermal transition curves, that is, the HS fraction γ_{HS} plotted as a function of temperature, which do not follow a simple Boltzmann distribution between two vibronic manifolds,[4] and strong deviations from first order kinetics in the HS $\rightleftarrows$LS relaxation.[5]

In a first chapter the influence of cooperative effects on both the spin-equilibrium as well as the relaxation kinetics are discussed qualitatively. In a second chapter the relaxation dynamics in the series of spin-crossover compounds $[Fe(Rtz)_6](BF_4)_2$, (Rtz = 1-alkyltetrazole) and $[Fe(pic)_3]Cl_2.EtOH$ (pic = 2-picolylamine) is being looked at, and in a third chapter the possibility of a light-induced bistability due to cooperative effects is considered. Complications arising in cases where the spin transition is accompanied by or due to a crystallographic phase transition[6,7] are not treated in this paper.

COOPERATIVE EFFECTS

For a spin-crossover system the zero-point energy difference $\Delta E^o_{HL} = E_{HS} - E_{LS}$ between the two states has to be positive and on the order of thermal energies. The entropy term in the free energy then drives the system to the HS state at elevated temperatures. The elastic interactions may be pictured as an internal or chemical pressure depending upon the distribution of complexes between HS and LS states. Electronically the complexes are still described individually, with the surroundings modulating ΔE^o_{HL}. In mean field approximation, this modulation only depends on the average number of complexes in a given state. A large fraction of small LS complexes leads to a contraction of the crystal lattice and thus to an increasing internal pressure which stabilises the LS state further, a large fraction of HS complexes, on the other hand, leads to an expansion and thus to a decreasing internal pressure which, in turn, stabilises the HS state (see Fig. 1). Therefore, transition curves in neat materials are generally steeper than in diluted mixed crystals,[4,8] and for values of the interaction parameter Γ above some critical value, a thermal hysteresis may even be observed.[9] By the same argument the HS ⇄ LS relaxation following a light-induced perturbation of the thermodynamic equilibrium[10] is self-accelerating.[5]

The concept of an internal pressure accounts for isotropic, long-range interactions only. Such long-range interactions in the form of an image pressure[11] are always present in finite crystals, and as shown above, tend to stabilise the majority species. In addition,

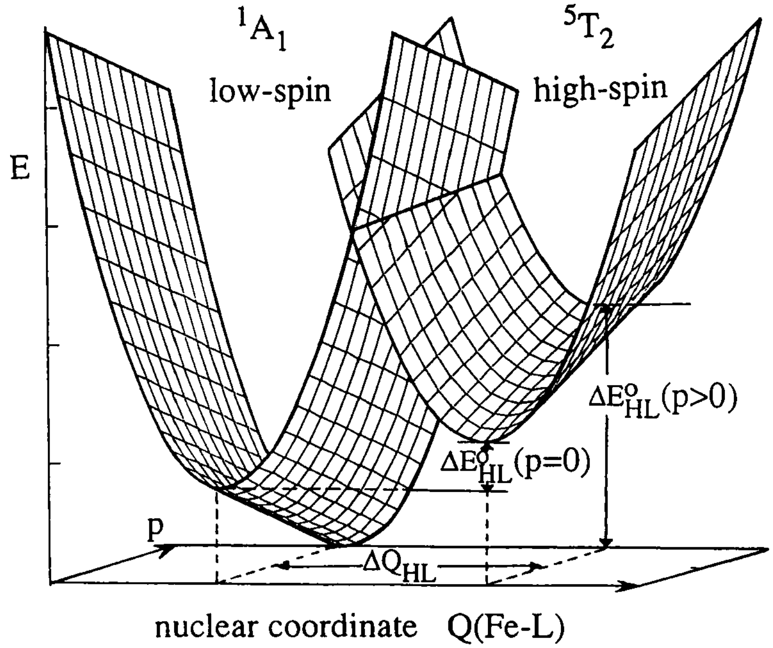

FIGURE 1 Schematic representation of the potential wells of the high-spin and the low-spin state in an iron(II) spin-crossover compound as a function of pressure. p stands for external pressure, but can also be interpreted as the build-up of an internal pressure due to elastic interactions.

direct, short-range interactions are important.[12] They can either reinforce the effect of the long-range interactions, in which case the two contributions to the interaction are very difficult to separate experimentally, or they can act in such a way as to favour the formation of HS-LS pairs.[13] This latter case may lead to steps in the thermal transition curves even for crystal structures where all complexes sit on crystallographically equivalent lattice sites.[14,15] Naturally, this also affects the HS $\rightleftarrows$ LS relaxation.

In systems for which the spin changing complexes sit on non-equivalent lattice sites, the spin transition of complexes on one site influences the behaviour of complexes on other sites. As is shown below, this effect gives rise to a light-induced bistability.

THE HS $\rightleftarrows$LS RELAXATION

It is possible to quantitatively populate the HS state below the thermal transition temperature as metastable state by irradiating either into the spin-allowed d-d or MLCT absorption bands of the LS species.[10] Fig. 2 shows the HS→LS relaxation curves following such an irradiation for $[Fe(ptz)_6](BF_4)_2$. The sigmoidal curves are well described phenomenologically by a relaxation rate constant depending upon the LS fraction according to:

$$k_{HL}(\gamma_{LS}, T) = k^{0}_{HL}(T) \exp(\alpha \cdot \gamma_{LS}), \tag{1}$$

that is, an exponential increase with increasing LS fraction. The initial rate constants $k^{0}_{HL}(T)$ are shown in Fig. 3a as Arrhenius plot, together with the rate constants for the HS→LS relaxation in a diluted mixed crystal $[Zn_{0.9}Fe_{0.1}(ptz)_6](BF_4)_2$ at 1 bar [16] and at 1 kbar external pressure.[17] The corresponding acceleration constants $\alpha(T)$ are shown in Fig. 3b. In addition, Fig. 3a contains the rate constants for the concentrated material at $\gamma_{LS} \rightarrow 1$ obtained from the full curves and from a partial (<10%) light-induced population

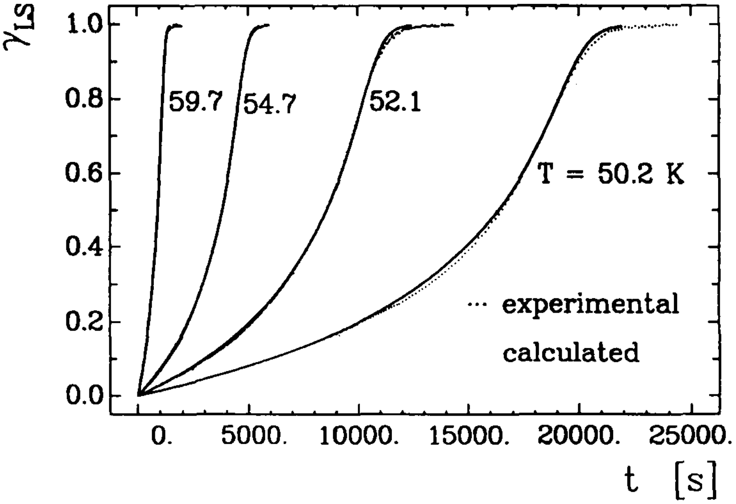

FIGURE 2 HS→LS relaxation curves for neat $[Fe(ptz)_6](BF_4)_2$ showing the recovery of the low-spin fraction following a quantitative light-induced population of the HS state, (···) experimental, (—) fit according to Eq.(1).

of the HS state only. The initial relaxation rate constants of the neat material are within experimental accuracy equal to the those of the diluted material at 1 bar. This is due to the ionic radius of iron(II) in the HS state being close to the one for zinc(II).

Both internal and external pressures accelerate the HS→LS relaxation. In fact, in analogy to Eq. (1) the rate constant as a function of external pressure p can be written as:

$$k_{HL}(T) = k_{HL}^{o}(T)\exp(\beta\cdot p). \qquad (2)$$

The acceleration factor β for the diluted material is included in Fig. 3b. Comparison of α and β shows that an external pressure of ~2 kbar would accelerate the relaxation in the diluted material by the same amount as the elastic interactions accelerate it in the neat

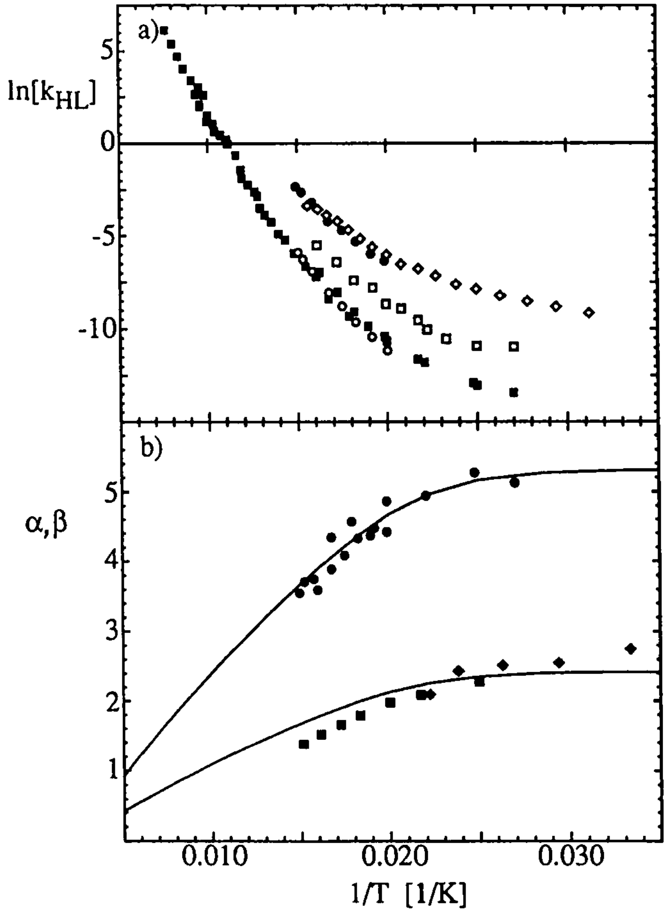

FIGURE 3 a) Initial and the final rate constants for the HS→LS relaxation in $[Fe(ptz)_6](BF_4)_2$ obtained from the full relaxation curves of Fig. 1, k_{HL}^{o} (o) and $k_{HL}^{o} + \alpha$ (•), and the final rate constant obtained after partial light-induced conversion to the HS state only (◊). HS→LS relaxation rate constants at 1 bar (■) and 1 kbar (□) for diluted $[Zn_{0.9}Fe_{0.1}(ptz)_6](BF_4)_2$. b) Acceleration factor α due to co-operative effects in $[Fe(ptz)_6](BF_4)_2$ (•) and acceleration factor β [$kbar^{-1}$] due to an external pressure in $[Zn_{0.9}Fe_{0.1}(ptz)_6](BF_4)_2$ (■) and $[Fe(ptz)_6](BF_4)_2$ (♦).

material. β behaves classically at temperatures above ~50 K, that is:

$$\beta(T) = -p\cdot\Delta V^{\#}_{HL}/k_BT, \tag{3}$$

The activation volume $\Delta V^{\#}_{HL}$ of -17 Å^3/complex is slightly larger in absolute terms than half the value of ΔV_{HL} of 26 Å^3/complex as obtained from pressure dependent equilibrium studies.[6] Below 50 K, β levels off to a limiting value of ~2.8 kbar^{-1}. At low temperatures the HS→LS relaxation is best described as nonadiabatic tunnelling process, for which the rate constant is given by the proportionality:[18]

$$k_{HL}(T\rightarrow 0) \sim \frac{S^n e^{-S}}{n!} . \tag{4}$$

The Huang-Rhys factor $S = \frac{1}{2} f \Delta Q^2_{HL}/\hbar\omega$ is a measure for the horizontal, the reduced energy gap $n = \Delta E^0_{HL}/\hbar\omega$ for the vertical displacements of the potential wells relative to each other. For iron(II) spin-crossover compounds a value for S of ~45 has been estimated [16] and n is on the order of one. In the strong vibronic coupling limit, that is for S >> n, Eq. (4) can be approximated as:

$$k_{HL}(T\rightarrow 0) \sim \exp(n\cdot\ln(S) - S) . \tag{5}$$

In principle, an external pressure changes both Δr_{HL} as well as ΔE^0_{HL}. The effect of the former is small compared to the latter, and with:

$$n(p) = n(p{=}0) + p\cdot\Delta V_{HL}/\hbar\omega = n(p{=}0) + p\cdot\beta_n , \tag{6}$$

the low temperature tunnelling rate constant as a function of pressure can be written as:

$$k_{HL}(T\rightarrow 0, p) = k_{HL}(T\rightarrow 0, p\rightarrow 0)\cdot\exp\{(\beta_n\ln(S) - \beta_S)p\}. \tag{8}$$

Thus $\beta(T\rightarrow 0) = \beta_n\ln(S) - \beta_S$. The first term corresponds to the increase in ΔE^0_{HL}, the second term accounts for the change in Δr_{HL} on the order of -10^{-3} Å/kbar. With the above value for S and $\hbar\omega = 250$ cm^{-1}, a value for $\beta(T\rightarrow 0)$ of ~2.5 kbar^{-1} has been estimated.[17] This is in good accordance with the experimental value.

The interpretation of the Eq. (1) for the rate constant as a function of γ_{LS} in the neat compound is now straight forward. The elastic interactions are well described by an internal pressure modulating ΔE^0_{HL} linearly with γ_{LS}. The acceleration factor of $\alpha(T\rightarrow 0)$ of ~5.2 corresponds to a difference in ΔE^0_{HL} of ~200 cm^{-1}. This is corroborated by the observed increase in the ligand field strength of the LS species during the relaxation,[5] and is related to the interaction constant Γ used to describe the thermal spin transition.[13]

The step in the thermal transition curve of [Fe(pic)$_3$]Cl$_2$·EtOH[14] has been attributed to nearest neighbour interactions favouring HS-LS pairs.[19] As for the above system, it is possible to achieve a quantitative light-induced population of the HS state at low temperatures and to record HS→LS relaxation curves (Fig. 4). At short relaxation times, that is for $\gamma_{HS} > 0.5$, they show the expected self-accelerating behaviour. Of course the system eventually ends up completely in the LS state, but for $\gamma_{HS} < 0.5$ the relaxation slows down again. This is thought to be due to a non-statistical process, in which nearest neighbour correlations build up as the relaxation proceeds.

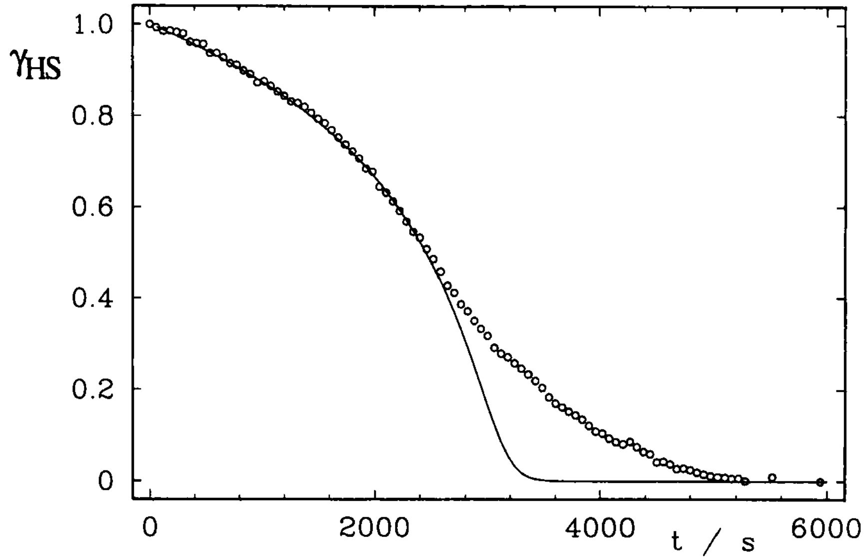

FIGURE 4 HS→LS relaxation curve showing the decay of the light-induced HS state in $[Fe(pic)_3]Cl_2 \cdot EtOH$ at 22 K, (o) experimental, (–) "best" fit according to Eq. (1) for $\gamma_{HS} > 0.5$. The slowing down for $\gamma_{HS} < 0.5$ is obvious.

LIGHT-INDUCED BISTABILITY

For negative values of ΔE^0_{HL}, that is with the HS state as quantum mechanical ground state of the system, no thermal spin transition is expected. In such cases it is possible to induce a spin transition by applying an external pressure which stabilises the LS state.[20] In neat materials, ΔE^0_{HL} is a function of γ_{LS}. Thus, even if at $\gamma_{LS} = 0$ the HS state is the true ground, an increasing internal pressure with an increasing LS fraction could stabilise the LS state sufficiently to result in it becoming the true ground state at $\gamma_{LS} = 1$. In this case, the system would be stable in the LS state at low temperatures. The only problem is, how to get there. The system in the HS state at ambient temperatures has no reason to populate the LS state on lowering the temperature because ΔE^0_{HL} at $\gamma_{LS} = 0$ is negative. However, at low temperatures the LS state can be populated photophysically by irradiating into the spin-allowed d-d absorption band of the HS species. Initially, this LS state is just a metastable state, but as the light-induced HS→LS conversion proceeds, ΔE^0_{HL} may become positive.

The $[Fe(etz)_6](BF_4)_2$ spin-crossover compound provides a convincing example of such a light-induced bistability.[21] In this system the iron(II) complexes sit on two non-equivalent lattice sites in a ratio of 2:1. Complexes on one site (denoted as site A) show a comparatively steep thermal spin transition with a transition temperature of 105 K, those on the other site (denoted as site B) stay in the HS state down to liquid helium temperatures (Fig. 5). Complexes on site A behave pretty much like in $[Fe(ptz)_6](BF_4)_2$ with regard to light-induced HS ⇄ LS conversions and relaxation processes. Those on site B can be converted quantitatively to the LS state at 20 K by irradiating at 820 nm, that is, into the $^5T_2 \rightarrow ^5E$ band of the HS species. A partial light-induced population of the LS state on the two sites results in an interesting relaxation behaviour at temperatures below 80 K: Complexes on site A always fully relax to the LS state irrespective of the initial LS fraction, because for them ΔE^0_{HL} is always positive. For initial values of $\gamma_{LS} < 0.3$, complexes on site B relax to the HS state, and the system ends up with the same overall LS fraction of ~2/3 as obtained by recording a straightforward transition curve (inset Fig. 5). For initial values of $\gamma_{LS} > 0.3$, however, site B complexes, too, relax to the LS state, so that the system ends up completely in the LS state. At temperatures below 80 K the cooperative effects thus result in the postulated light-induced bistable behaviour on site B.

As the temperature is raised to above 80 K, site B complexes go back to the HS state. This can be regarded as the thermal spin transition in heating mode of a system with a very large hysteresis, the corresponding branch in cooling mode not being accessible in a simple temperature cycle.

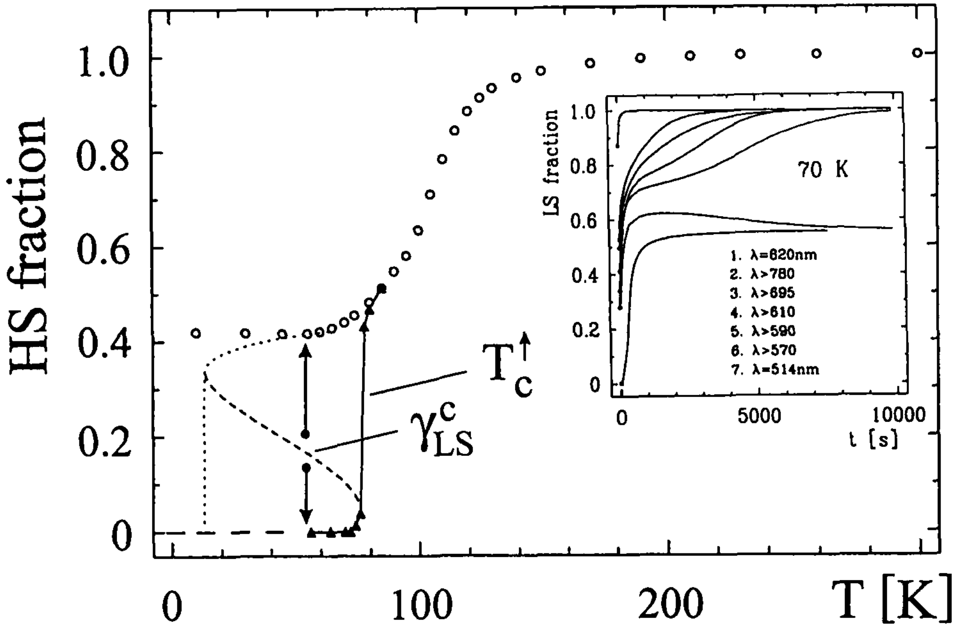

FIGURE 5 Thermal spin transition in [Fe(etz)6](BF4)2, (o) normal cooling mode, (▲) heating mode after irradiation at 820 nm. Inset: HS-LS relaxation curves following irradiation conditions resulting in different initial overall LS fractions.

CONCLUSIONS

Cooperative effects, in particular if they lead to bistable behaviour, are important for an number of applications, for instance in data storage and processing.[22] Spin-crossover compounds possess the basic ingredients necessary for optical devices, namely the possibility for switching between two states using light of different wavelengths. Unfortunately, the light-induced HS states are always metastable states, and although they may have lifetimes of up to ten days at liquid helium temperatures, at T > 50 K the relaxation invariably becomes faster. A fundamental understanding of the nature of the cooperative effects in spin-crossover compounds and their influence on both the thermal spin transition as well as the relaxation dynamics is thus of more than just academic interest. The above examples illustrate several aspects and consequences of these effects.

ACKNOWLEDGEMENTS

This work was financially supported by the "Schweizerischer Nationalfonds", the "Deutsche Forschungsgemeinschaft" and the "Portlandcement-Stiftung".

REFERENCES

1. a) P. Gütlich, Structure and Bonding 44, 83 (1981), b) J. K. Beattie, Adv. Inorg. Chem. 32 , 1 (1988). c) E. König, Structure and Bonding 76, 51 (1991). d) P. Gütlich, A. Hauser, H. Spiering, Angew. Chemie (Int. Ed. Engl.) 33, 2024 (1994).
2. a) M.A. Hoselton, L.J. Wilson, R.S. Drago, J. Amer. Chem. Soc. 97, 1722 (1975). b) M. Mikami-Kido, Y. Saito, Acta Cryst B38, 452 (1982). c) B. A. Katz, C. E. Strouse, J. Amer. Chem. Soc. 101, 6214 (1979). d) B. Gallois, J. A. Real, C. Hauw, J. Zarembowitch, Inorg. Chem. 29, 1152 (1990).
3. a) L. Wiehl, H. Spiering, P. Gütlich, K. Knorr, J. Appl. Cryst. 23, 151 (1990). b) L. Wiehl, G. Kiel, C.P. Köhler, H. Spiering, P. Gütlich, Inorg. Chem. 25, 1565 (1986). d) R. A. Binstead, J. K. Beattie, Inorg. Chem. 25, 1481 (1986).
4. H. Spiering, E. Meissner, H. Köppen, E. W. Müller, P. Gütlich, Chem. Phys. 68, 65, (1982).
5. A. Hauser, Chem. Phys. Lett. 192, 65 (1992).
6. J. Jeftić, R. Romstedt, A. Hauser, to be published in J. Phys. Chem. Solids.
7 L. Wiehl, Acta Cryst B49, 289 (1993).
8. J.-P. Martin, J. Zarembowitch, A. Dworkin, J. G. Haasnoot, E. Codjovi, Inorg. Chem. 33, 2617 (1994).
9. C. P. Köhler, R. Jakobi, E. Meissner, L. Wiehl, H. Spiering, P. Gütlich, J. Phys. Chem. Solids 51, 239 (1990).
10. a) S. Decurtins, P. Gütlich, K. M. Hasselbach, H. Spiering, A. Hauser, Inorg. Chem. 24 , 2174 (1985). A. Hauser, J. Chem. Phys. 94, 2714 (1991).
11. J. D. Eshelby, in Solid State Physics Vol. 3 (Academic, New York 1956) p. 79.
12. a) N. Willenbacher, H. Spiering, J. Phys. C 21, 1423 (1988). b) H.Spiering, N. Willenbacher, J. Phys.: Condens Matter 1, 10089 (1989).
13. J. Jung, G. Schmitt, L. Wiehl, A. Hauser, K. Knorr, H. Spiering, P. Gütlich, to be published in Zeitschrift für Physik B.
14. H. Köppen, E. W. Müller, C. P. Köhler, H. Spiering, E. Meissner, P. Gütlich, Chem. Phys. Lett. 91, 348 (1982).
15. J. A. Real, H. Bolvin, A. Bousseksou, A. Dworkin, O. Kahn, F. Varret, J. Zarembowitch, J. Amer. Chem. Soc. 114, 4640 (1992).
16. A. Hauser, A. Vef, P. Adler, J. Chem. Phys. 95, 8710 (1991).
17. J. Jeftić, A, Hauser, Chem. Phys. Lett. 248, 458 (1996).
18. C. J. Donnelly, G. F. Imbush, G. F., in NATO ASI B245 (ed. B. DiBartolo, Plenum Press, New York, 1991) p. 175.
19. R. Jakobi, H. Spiering, P. Gütlich, J. Phys. Chem. Solids 53, 267 (1992).
20. a) J. Zarembowitch, C. Roux, M.-L. Boillot, R. Claude, J. P. Itie, A. Polian, M. Bolte, Mol. Cryst. Liq. Cryst Sci. Technol. A 234, 247 (1993). b) J. K. McCusker, M. Zvagulis, H. G. Drickamer, D. N. Hendrickson, Inorg. Chem. 28, 1380 (1989).
21. R. Hinek, P. Gütlich, A. Hauser, Chemistry - a European Journal, submitted.
22. J. Kröber, E.Codjovi, O.Kahn, F.Grolière, C.Jay, J. Amer. Chem. Soc. 115, 9810 (1993).