Spin Crossover

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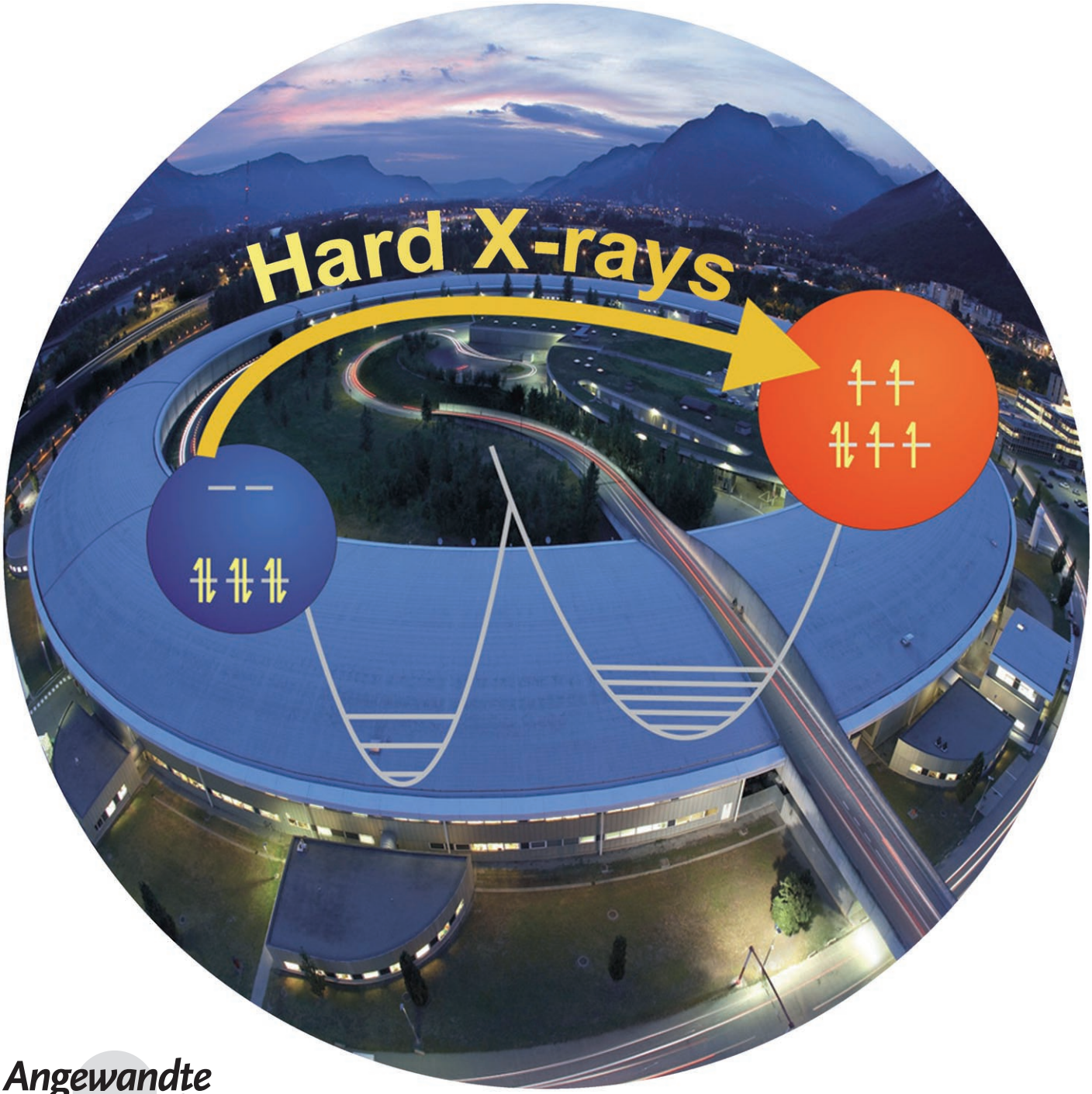
Hard-X-ray-Induced Excited-Spin-State Trapping**

György Vankó, Franz Renz,* Gábor Molnár, Thomas Neisius, and Szilvia Kárpáti*



More than 20 years ago, it was discovered that thermally switchable iron(II) spin-crossover complexes can also be switched optically from the low-spin (LS) ^1A_g state to a long-lived metastable high-spin (HS) $^5T_{2g}$ state at low temperatures.[1] The understanding of this phenomenon, known as light-induced excited-spin-state trapping (LIESST), paved the way to intriguing insights into the electronic structure. Later it was revealed that this metastable state can be reached in a strikingly different way. This discovery was made when an anomalous HS state was observed in the Mössbauer emission spectra after the $^{57}Co(EC)^{57}Fe$ nuclear decay (EC = electron capture).[2,3] This nuclear-decay-induced phenomenon was called NIESST, in analogy to LIESST.

Similar molecular effects provoked by hard X-rays have not been reported to date, albeit phase transitions occurring on irradiation with hard-X-ray beams have been found in a few inorganic solids, such as manganites or Prussian-blue analogues.[4] Herein, we report on the remarkable effect of hard-X-ray-induced excited-spin-state trapping (HAXIESST) in the molecular iron(II) spin-crossover complex $[Fe^{II}(phen)_2(NCS)_2]$ (**Fe^{II}**; phen = phenanthroline).[5] The long-lived metastable HS states in LIESST and HAXIESST show similar spectroscopic behavior and their formation and decay conditions suggest similar mechanisms. This result shows that it is important to be aware of the non-innocent nature of X-rays in investigations, especially at low temperatures, and also suggests a possible use of X-rays as an alternative excitation source of high efficiency and large penetrating power.

We recently studied **Fe^{II}** and also the complex $[Fe^{III}(L)py]BPh_4$ (**Fe^{III}**; py = pyridine, L = bis(3-salicylidene aminopropyl) amine)[6] at temperatures of 80–300 K and demonstrated that Kβ X-ray emission spectroscopy (XES) can be used to quantitatively monitor the spin-state changes that accompany thermally induced spin crossover.[7] Herein, we extend the XES study of **Fe^{II}** and **Fe^{III}** to lower temperatures; we use the same technique to explore possible excitations in a lower temperature region. XES is a direct probe of the number of unpaired electrons in the 3d orbitals and, thus, of the spin state.[7–9] In an XES experiment a 1s core hole is created by ionization with the X-ray beam. The Kβ spectrum is generated from X-rays emitted in the subsequent transition when an electron from a 3p orbital fills the core hole; the characteristic sensitivity to the spin state stems from the strong 3p–3d exchange interaction in the final state. The conversion from the LS into the HS state is indicated by an increase in the intensity of a low-energy satellite (Kβ′) to the main peak and by a shift of the main peak to higher energy.

Herein, we apply XES to the study of **Fe^{II}** and **Fe^{III}** below 80 K, where both are in the LS ground state. Low-enough temperatures provide an opportunity to seek X-ray-induced excitations, in analogy to LIESST, as they can lead to "frozen" metastable states. At 80 K, no HS contribution was detected in the spectrum of either compound. Below this temperature **Fe^{III}** remained in the LS state, as expected (Figure 1, right).[2,10] However, an anomalous behavior was found for

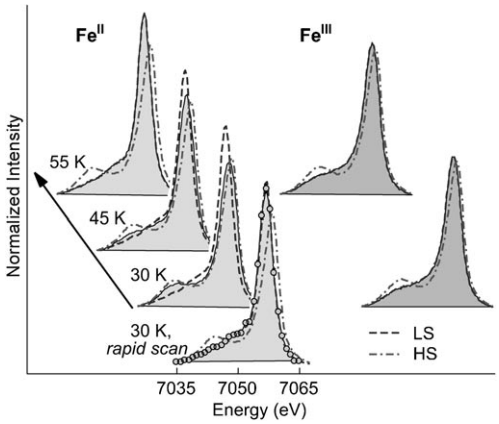


Figure 1. Kβ spectra of **Fe^{II}** (left) and **Fe^{III}** (right) at low temperatures, represented as curves with their areas filled. Reference spectra for the pure LS (-----) and HS (–•–•), measured at 80 and 295 K, respectively, are also plotted for each spectrum. Also shown is a rapid scan at 30 K, which was performed without previous exposure to X-rays (○).

Fe^{II}: whereas a rapid (20 s) scan at 30 K still confirmed the LS state, in a long (15 min) scan, after several minutes exposure to the beam, the Kβ′ satellite appeared and a spectral shift occurred (Figure 1). Both features indicate that the majority of the sample transformed to the metastable HS state in the beam. Line-shape analysis revealed a high-spin fraction of 72% and a repeated scan showed no further change of the HS population. Similar observations of anomalous metastable HS states detected for the same compound upon irradiation with green light[11] and soft X-rays[12] at low temperatures were interpreted as excited-spin-state trappings, LIESST and SOXIESST, respectively. To check whether a similar scenario applies to our case, we studied the temperature dependence

[*] Dr. G. Vankó
European Synchrotron Radiation Facility
BP 220, 38043 Grenoble Cedex (France)
and
KFKI Research Institute for Particle and Nuclear Physics
P.O. Box 49, 1525 Budapest (Hungary)
Fax: (+33) 476-882-624
E-mail: vanko@esrf.fr
Prof. Dr. F. Renz
Institut für Anorganische Chemie und Analytische Chemie
Johannes Gutenberg-Universität Mainz
Duesbergweg 10–14, 55099 Mainz (Germany)
Fax: (+49) 6131-392-6626
E-mail: Franz.Renz@uni-mainz.de
Dr. G. Molnár
Laboratoire de Chimie de Coordination
CNRS UPR-8241205 route de Narbonne
31077 Toulouse (France)
Dr. T. Neisius
CP2M, Faculté des Sciences et Technique
Université Paul Cézanne
Aix-Marseille III, 13397 Marseille Cedex 20 (France)
S. Kárpáti
Department of Nuclear Chemistry
Eötvös Loránd University
Pázmány sétány 1A, 1118 Budapest (Hungary)

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of the metastable HS contribution. Upon increasing the temperature, a lower X-ray-induced metastable HS contribution was observed: a metastable HS contribution of 42% was measured at 45 K, and the HS signal completely disappeared at 55 K. This decay temperature corresponds well to what was observed for the visible-light-induced metastable state.[13] Upon heating to above 176 K, the sample was converted into the thermal HS state, and the entire "stable HS"→LS→"metastable HS" conversion cycle was reproduced on the same spot. These results all indicate that the effect is fully reversible. The vanishing of the HS fraction upon heating excludes the possibility of artifacts arising from local heating or decomposition caused by the X-ray beam. This conclusion is further supported by the fact that no such anomalous HS contribution was observed in the spectra of **Fe^{III}** (Figure 1, right), as these spectra reflect a pure LS state at low temperatures.

All our findings are in accordance with what is expected for a metastable-spin-state trapping. The LIESST phenomenon occurs because the relaxation of the photoexcited HS state is impeded at low temperatures. The direct transition ($^5T_{2g}\rightarrow{}^1A_g$) is spin-forbidden; the path of intersystem crossings, which could bring the system back to the LS ground state, is hindered below 50 K, as the relevant vibrational modes are inactive, which makes the tunneling rate between the HS and LS states very small for this type of Fe^{II} compound.[14] These features all make the lifetime of the excited state practically infinite at low-enough temperatures. In our case, the form of excitation is different, the spin-state trapping most likely occurs in the relaxation processes that follow electronic excitations caused by secondary electrons, similar to that in nuclear decay.[3] However, while in NIESST the excitation is reached after a cascade of electronic transitions (which includes multiple core and valence ionizations and the following neutralization processes), in HAXIESST the vast majority of the iron atoms experience only a valence excitation before the probing quantum arrives; the excitation in this case occurs through secondary electrons originating from a remote ionization.

Consequently, we can conclude that low-temperature X-ray investigations, whether spectroscopic or diffraction, might lead to population of the long-lived metastable HS state of spin-transition compounds. This result also suggests that in photoswitchable systems, excitations similar to visible-light-induced ones might be observed when the sample is exposed to an intense X-ray beam at low temperatures. Accordingly, a large lattice response to X-ray diffraction has recently been reported for a photoswitchable Prussian-blue analogue.[4b]

Many details of the HAXIESST effect are yet to be investigated: for example, the temperature, X-ray intensity, and energy dependence of the phenomenon as well as its evolution in time. As the excitation is not selective, a reverse effect is also anticipated. This investigation should also provide an opportunity to study whether the populations follow branching ratios observed in light-excitation studies, or if they are higher as was found after the excitations of the nuclear decay.[15] The reasons for the overly high populations of the metastable HS state in NIESST and for the existence of a strong-field (SF) Fe^{II} complex showing SF-LIESST[16] are disturbing open questions in the field of molecular magnetism. Both LIESST and SF-LIESST are single-molecular effects, as shown by metal-dilution experiments;[2,16] the decay behavior of the HAXIESST state points to a single-molecular effect. The suggested investigations might give further insight into the electronic structure of these materials, including a deeper understanding of the apparent differences in the mechanism and dynamics of the relaxation processes that follow different excitations.

Finally, we propose that irradiation with hard X-rays can be exploited to populate metastable states when optical excitation is limited by the characteristics of the sample or by its environment, as in the cases of nontransparent samples or under extreme conditions. Hard X-rays can be a good alternative to excitation with visible light, because NIESST necessitates radioactive samples where the "excitation" is uncontrollable and chemical after-effects can arise from the nuclear decay, and soft X-rays lack penetration power and are unlikely to outperform laser excitations.

Experimental Section

The **Fe^{II}** (polymorph I) and **Fe^{III}** samples were prepared as described in refs. [5] and [6], respectively; they have been characterized by elemental analysis, magnetic susceptibility, and Mössbauer spectroscopy. The experiment was performed on a 1 m arm Rowland-circle IXS spectrometer at beamline ID26 of the European Synchrotron Radiation Facility (ESRF). The flux of the incident beam after the cryogenically cooled Si(111) monochromator was about 10^{13} photons s^{-1}, distributed over a spot of 0.3×1 mm^2.

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