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Neutron Laue diffraction on the spin crossover crystal $[Fe(1\text{-}n\text{-propyltetrazole})_6](BF_4)_2$ showing continuous photoinduced transformation

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The structural aspects of photoinduced phase transitions in spin-crossover compounds were investigated by neutron Laue diffraction. The structures of the ground state and of the metastable LIESST state of the Fe^{II} spin transition compound $[Fe(1\text{-}n\text{-propyltetrazole})_6](BF_4)_2$, in the quenched state, were determined at 2 K. Sizable differences are observed between the photoinduced and the high-temperature high-spin structures. The structural changes were observed to be continuous, despite the cooperative character of the spin-crossover system, and their kinetics was followed during the photoexcitation at 2 K. The reasons why the nucleation and growth process reported in the literature does not apply here are examined.

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The field of molecular magnetism has recently received additional motivation courtesy of the development of new compounds possessing properties that can be controlled and tuned by light, pressure, or magnetic field. The ability to control externally the magnetic, optical, and electronic nature of these compounds makes them suitable for applications in information storage and optical switching. Among these switchable solids, spin-crossover (SC) compounds have been studied extensively, up to the design of a thermocontrolled numerical display.[1] The photoswitching process of the spin states was so far reported to have a single-molecule character[2] which makes possible the complete population of the metastable high-spin (HS) state at low temperature, according to the so-called light induced excited spin state trapping (LIESST).[3] This process and the subsequent relaxation of the metastable spin state were elucidated mainly by magnetic, photomagnetic, Mössbauer and optical spectroscopies.[4] Until recently, all experiments performed on SC compounds at low temperature and with weak sources of light, e.g.,[5] led to kinetic data consistent with the single-molecule model.

The solid state aspects of the photoexcitation process were recently studied by x-ray diffraction.[6–8] On the one hand, the existence of spinlike domains, i.e., domains of high-spin molecules and low-spin molecules was evidenced both at the thermal and photoinduced transitions, on SC solids[6–10] and Prussian Blue analogues[11,12] exhibiting charge-transfer-induced spin transition (CTIST).[13] Indeed demixtion, i.e., the phase separation into spinlike domains, was already suggested in previous experimental works on the light-induced instability of SC compounds under light,[14–16] in the temperature range where self-accelerated relaxation[17] efficiently competes against the photoexcitation process. On the other hand, structural differences between the photoinduced and thermally induced high-spin phases have been reported in some cases[18] and are considered as another "hot topic" in the field of molecular switchable solids.

We report on the first application of the neutron Laue diffraction technique to the investigation of the structural aspects of the photoinduced spin transition in $[Fe(ptz)_6](BF_4)_2$ (ptz=1-n-propyltetrazole). This compound is the most prominent member of this class of spin-crossover compounds. $[Fe(ptz)_6](BF_4)_2$ in the quenched phase (see below) has been studied extensively and particularly its cooperative relaxation[19] and photoexcitation[20] properties and photostationary states.[21] All this knowledge was the reason for selecting this "typical" SC compound $[Fe(ptz)_6](BF_4)_2$.

Single crystals of $[Fe(ptz)_6](BF_4)_2$ in the form of hexagonal plates were obtained by slow evaporation from a saturated nitromethane solution.[22] According to Ref. 21, $[Fe(ptz)_6](BF_4)_2$ crystallizes in the trigonal $R\bar{3}$ space group; $a=b=10.720(1)$ Å, $c=31.640(1)$ Å, $\gamma=120°$. An abrupt and spin transition takes place at $T_c=130$ K, with color (light purple to transparent) changes, while the rhombohedral structure is kept. Upon slow cooling, the spin transition is normally accompanied by a crystallographic phase transition ($R\bar{3}$ to $P\bar{1}$) with an hysteresis of 7 K ($T_c\downarrow=128$ K and $T_c\uparrow=135$ K), but this phase transition can besuppressed by quenching the sample in liquid nitrogen.[16] The LIESST ($LS\rightarrow HS$) effect is generated by dc sources of light in the 450–550 nm range. At 2 K, the lifetime of the photoinduced state is several weeks and irradiation can be switched off when photoexcitation has been completed. On increasing temperature, relaxation of the metastable HS state becomes sizeable. In the presence of light, the spin equilibrium is governed by the competition between relaxation and photoexcitation. Above 50 K relaxation dominates photoexcitation, for example, the lifetime of the photoexcited HS state drops down to ~150 s at 67 K, which totally hinders the

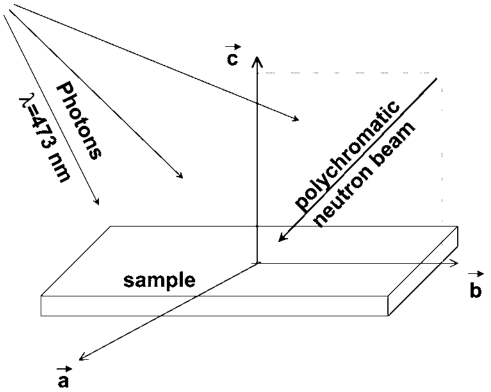

FIG. 1. Relative orientation of the neutron beam, laser beam, and crystallographic axes in the experimental setup.

photoexcitation effect when continuous sources of light are used.

A photocrystallographic experimental setup has been installed on VIVALDI, Very Intense Vertical Axis Laue Diffractometer, at the Institut Laue Langevin. The VIVALDI instrument uses a white beam of neutrons in the wavelength range 0.8–5.2 Å and a cylindrical image plate which collects diffracted intensities over a solid angle of ~8 steradians. It is especially suitable for small-molecule samples[23] and relatively small crystals. Compared to conventional monochromatic diffractometers, VIVALDI experiments are considerably shorter (ca. 1–3 days instead of 1–2 weeks).

A $[Fe(ptz)_6](BF_4)_2$ single crystal, with a platelet shape $2\times 2\times 0.1$ mm^3, was set on the diffractometer in the geometry described in Fig. 1. The sample was quenched down to the liquid helium temperature, within ~5 minutes, and the expected rhomboedric phase was indeed observed. The sample was submitted to a low intensity of 2 mW/cm^2 coming from the laser source (473 nm, 30 mW). The working wavelength ($\lambda = 473$ nm) is smaller than that of the LS state absorption peak (~550 nm), which reduces the inhomogeneous character of the photoexcitation process associated with the bulk absorption of light in the sample. Hence a complete photoexcitation is possible. Furthermore, the low value of the laser intensity ensured that the temperature increase of the sample under illumination remained moderate, far below 1 K, as estimated from previous studies on the same or similar photoswitchable compounds.[24,25]

In order to follow the kinetics of the photoexcitation process at 2 K, a series of Laue patterns were recorded, after different irradiation times, with the light switched off and a neutron exposure time of 20 minutes. The saturation was reached after about 2 hours of light irradiation time. The sizable shift of the spots towards the center is shown in Fig. 2, and agrees with the expected volume increase upon the LS → HS transition.[8] The kinetics of the photoswitching is in good agreement with the previous photomagnetic data,[2,26] once the differences in the specific intensities and wavelengths are accounted for.

The detailed investigations in the initial and in the phototransformed states were performed on the basis of six different Laue patterns, each accumulated over 3 hours, collected at 20° intervals in rotation of the crystal about the vertical axis of the cylindrical detector, at 2 K. A total of 2887 and 3497 reflections, of which 760 and 1007 were independent, were recorded for the ground and photoinduced states, respectively. The reflections were indexed and the orientation defined using the program LAUEGEN.[27] The peaks were integrated and the background removed using the program ARGONNE BOXES.[28] The intensities for each state were normalized by comparison of repeated and symmetry equivalent reflections, to a constant incident wavelength using the program LAUENORM;[29] only reflections observed at wavelengths in the range 0.8–5 Å were accepted in this step. Subsequent calculations for structure determination were carried out using the CRYSTALS package. Initial atom positions were obtained from earlier x-ray structure determinations of the high temperature HS phase and of the low temperature LS phase.[20] Least-squares refinement of all atomic coordinates and isotropic temperature factors resulted in a final agree-

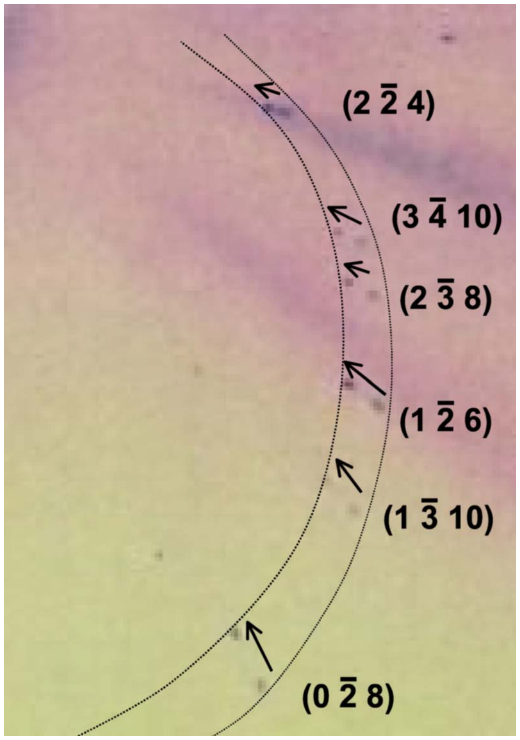

FIG. 2. (Color online) Partial view of a superposition of two Laue patterns of $[Fe(ptz)_6](BF_4)_2$ at 2 K, before and after illumination (473 nm, 2 mW/cm^2, 2 h), showing the inwards shift of the Bragg spots upon phototransformation.

TABLE I. Selected crystallographic data.

	LS $T=2$ K	Photoinduced HS $T=2$ K	High Temp. HS $T=195$ K
$d_{\text{Fe-N}}$ (Å)	1.98(1)	2.18(1)	2.180(3)
N-Fe-N[a]	89.8(6)	89.7(4)	89.5(1)
N-Fe-N[b]	90.2(6)	90.3(4)	90.5(1)
Reference	This work	This work	Ref. 22

[a] Parallel to $(\mathbf{a},\mathbf{b})$ plane.

[b] Perpendicular to $(\mathbf{a},\mathbf{b})$ plane.

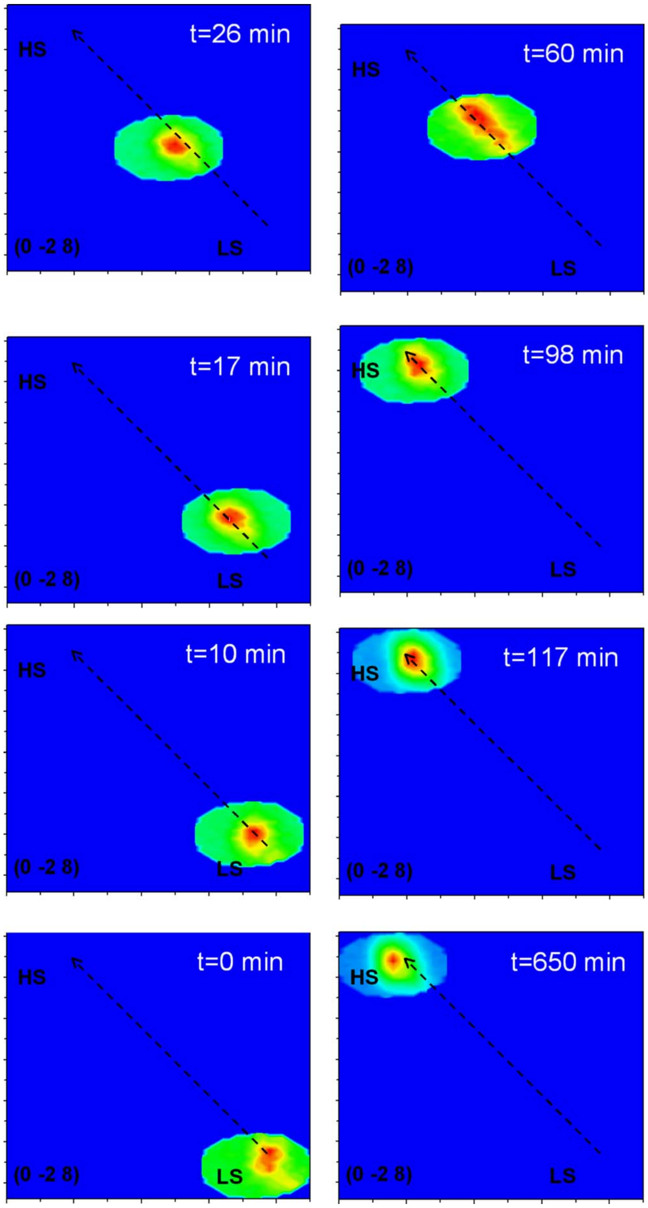

FIG. 3. (Color online) Shift of the $(0,-2,8)$ reflection of $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ upon photoexcitation at 473 nm, 2 K.

ment factor of $R(F^2)=11.7\%$ for 337 independent reflections with $I>3\sigma(I)$ for the ground state and $R(F^2)=9.9\%$ for 395 independent reflections with $I>3\sigma(I)$ for the photoinduced state. Since only the ratios between unit-cell dimensions can be determined in the white-beam Laue technique, x-ray cell dimensions at 10 K were used in the neutron refinements.[8] The complete set of crystallographic data is given as complementary material. Essential data concerning the molecular geometry in the respective low temperature LS, LIESST-HS and high temperature HS states are listed in Table I. The major results are discussed below.

(i) *Structure of the photoinduced phase*: The Fe-N distance is increased by 0.21 Å, the unit-cell volume by about 2%, all other interatomic distances remaining the same in the molecule. These data are in excellent agreement with the previous reports on the same compound by Kusz *et al.*[10] and on other $\mathrm{Fe^{II}}$ SC solids: X-ray diffraction[6,7] of $[\mathrm{Fe(2\text{-}pic)_3}]\mathrm{Cl_2EtOH}$ showed an elongation of the Fe-N bond lengths by ~0.2 Å, and XANES and EXAFS data showed an essentially isotropic expansion of the octahedral core of $[\mathrm{Fe(2\text{-}pic)_3}]\mathrm{Cl_2EtOH}$.[30] The local geometry of the Fe ion in the photoinduced and high temperature (= thermally induced) high-spin phases seems to be close (see Table I). The question of the relative stabilities of these high-spin phases should be adressed. We speculate that the lack of thermal excitations during the building-up of the raw photoinduced phase at low temperature may result in its metastable character (with respect to structural evolutions), like observed in Prussian Blue analogs when photoinduced magnetic structures are created at low temperature.[31]

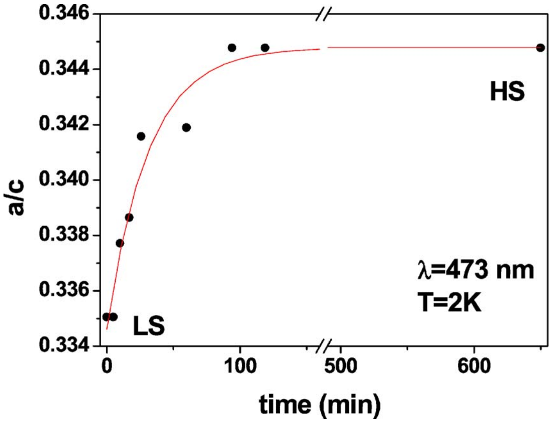

FIG. 4. (Color online) Kinetics of the photoexcitation of $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ at 473 nm, 2 K followed on the cell parameters a/c ratio. Data are tentatively fitted by a single exponential law.

(ii) *Reassessment of the spin-density map*: Previous polarized neutron measurements on the 5C1 diffractometer at the LLB on a $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ single crystal provided the first spin-density map, at 2 K, of the photoinduced state,[29] using a similar photomagnetic experimental setup. However this map was obtained using crystallographic parameters from x-ray experiments.[6] The present determination of the photoinduced structure at 2 K permits a more precise polarised neutron data analysis and confirm the main features of the previous spin density map. The determination of the $\mathrm{Fe^{2+}}$ magnetic moment in the photoinduced electronic state is improved. The refined value of the $\mathrm{Fe^{2+}}$ magnetic moment, 3.75(10) μ_B [instead of 4.05(7) μ_B in Ref. 26], is closer to the value determined by magnetic measurements, $3.85\mu_B$,[26] and to the calculated value of the spin contribution of the $\mathrm{Fe^{2+}}$ state, $3.84\mu_B$ ($S=2$ at 2 K,5 Tesla). No significant spin densities are observed on the nitrogen atoms.

(iii) *Progressive character of the photoinduced phase transformation*: The evolution of the $(0,-2,8)$ Laue spot, as a function of the total irradiation time, is shown in Fig. 3. The observed continuous shift clearly rules out the nucleation and growth of like-spin domains in the phase transformation. It also shows the basically homogeneous character of the photoexcitation process, which requires that the penetration depth of light is in large excess of the crystal size at all stages of irradiation, i.e., irrespective of the bleaching process which facilitates the complete photoexcitation. The ab-

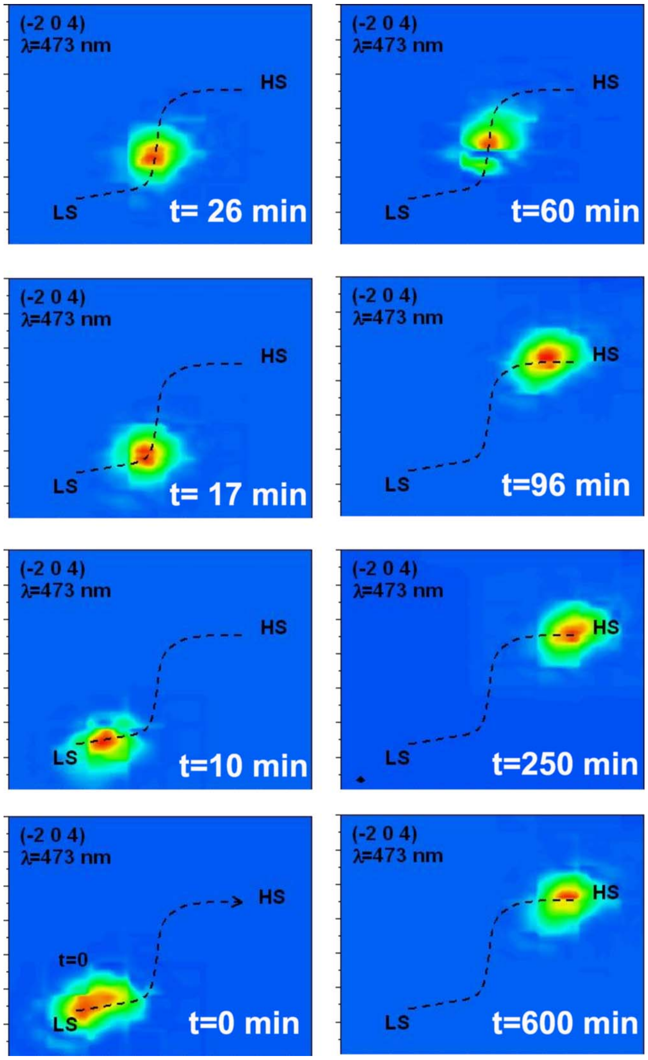

FIG. 5. (Color online) Shift of the $(-2,0,4)$ reflection of $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ upon photoexcitation at 473 nm, 2 K.

sence of like-spin domains in the present cooperative spin-crossover system can be understood by considering the nature of the driving force for the nucleation and growth process. In the mean-field approach we developed in previous works,[12,13] demixtion is driven by the bistability of the photostationary states due to competition between photoexcitation and self-accelerated relaxation rates. At low temperature, relaxation is slow and photoexcitation results in a completely saturated HS state. However, above ~45 K, in the temperature range where the light-induced bistability has been observed,[18] nucleation mechanism and coexistence of two phases (LS and HS) in $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ can be expected in the quenched structural phase. A further reason for the hindrance of the nucleation and growth process at low temperature is the weakness of the diffusion processes. At last, we have reported in Fig. 4 the evolution of the a/c ratio, that we tentatively compare to the single exponential variation of the HS population expected in the case of constant photoexcitation rate when both HS → LS relaxation and bulk absorption of light are negligible.

In conclusion, nuclear structures of the ground state and of the metastable LIESST state of the spin transition compound $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ were determined at 2 K by neutron Laue diffraction. The results show that the local structure variation upon photoinduced spin transformation is essentially an expansion of the Fe-N_6 core without lowering of the O_h symmetry of Fe environment. The Fe-N distance is increased by 0.21 Å and the unit-cell volume by about 2%. We found that the local structure of the photoinduced phase is very close to that of the high temperature high spin state. For the first time, a progressive character of the photoinduced phase transformation was evidenced in spin-crossover compounds. Further investigation of several Laue spots during irradiation revealed departures from the linear pathway reported in Fig. 3. For example, the plot of the $(-2,0,4)$ spot, see Fig. 5, showed a Z-shaped pathway associated with a clear slowing down of the motion of the spot, at roughly midway. We therefore are led to speculate that the response of the structure to the photoinduced increase in HS population is far from linear. An accurate determination of the structure at all stages of photoexcitation is needed to document this amazing issue.

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