Multimetastability, phototrapping, and thermal trapping of a metastable commensurate superstructure in a Fe\(^{II}\) spin-crossover compound

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The photoinduced switching and subsequent relaxation regime at cryogenic temperatures of the two-step spin-crossover compound [Fe(bapbpy)(NCS)\(_2\)] has been investigated by time-dependent photocrystallography. Upon photoexcitation from the low-spin (LS) state, a direct population of the metastable high-spin (HS) state occurs, without involving any intermediate structural state. The relaxation from the metastable HS state in isothermal conditions at 40 K proceeds in two successive steps associated with two symmetry breaking processes. The first step corresponds to the cooperative transformation to an intermediate superstructure, characterized by a long-range-ordered [HS-LS-LS] motif coupled to a commensurate displacive modulation, and concomitant with a tripling of the c axis of the unit cell (C\(_2\)/c space group). The stabilization of the intermediate state is driven by strong molecule-lattice coupling. In the second stage, the intermediate state undergoes a transformation twinning triggered by lattice strain towards the LS state. The two-step relaxation is reminiscent of the two-step thermal transition of [Fe(bapbpy)(NCS)\(_2\)] and evidences multimetastability in the light-induced or relaxation regime. The long-range-ordered [HS-LS-LS] superstructure has also been trapped by rapid quench cooling to very low temperature, and has been structurally characterized.

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I. INTRODUCTION

Spin-crossover (SCO) complexes are one of the most intensively studied molecular switchable materials;\(^1\) their relevance in the conception of novel magnetic or optical devices presently stimulates much research effort.\(^2\) For Fe\(^{II}\) SCO systems, the reversible switching between the high-spin (HS, \(S = 2\)) and the low-spin (LS, \(S = 0\)) molecular states is accompanied by drastic changes in optical, magnetic, and dielectric properties, and may be triggered by a variation of temperature or pressure, by guest molecule inclusion, or by light irradiation. This latter process, called LIESST\(^3\),\(^4\) (light-induced excited spin-state trapping), consists of a conversion from the thermodynamically stable LS state to a metastable HS state with the extended lifetime below the limiting temperature \(T\) (LIESST).\(^5\) The essential characteristics of the spin transition strongly depend on the cooperativity, which results from the local structural distortion associated with the molecular spin state change (HS-LS molecular volume change in a first approximation), coupled to long-range interactions of elastic origin in the crystalline solid. These interactions are mediated by intermolecular contacts, such as hydrogen bonds, \(\pi-\pi\) contacts, and van der Waals interactions within the crystal lattice, sometimes assisted by lattice solvate molecules or counterions. Strong cooperativity favors abrupt thermal transitions, possibly of first order with a hysteresis loop, as well as HS→LS nonlinear sigmoidal relaxation curves following light-induced population of the HS metastable state.\(^6\) The mean-field approximation may well describe most of the spin transition properties in the thermal transition (quasistatic) and LIESST (dynamic) regimes.\(^7\),\(^8\) Short-range correlations may also compete with long-range interactions and give rise to deviation from mean-field behaviors,\(^9\) as evidenced in some cases by distinctive long relaxation tails from the LIESST state.\(^10\)

Although the vast majority of thermal spin transitions proceed in a single step, there has been an increasing number of two-step transitions reported for polymeric,\(^11\)–\(^17\) polynuclear,\(^18\)–\(^24\) or mononuclear SCO systems.\(^25\)–\(^44\) Such transitions result most frequently from the existence of two crystallographically (symmetrically) independent SCO Fe\(^{II}\) sites with slightly different coordination environments, leading to dissimilar transition temperatures delimiting a plateau (or shoulder), which usually occurs with an approximately equal populations of HS and LS species. Alternatively, the subtle interplay between short-range correlations and long-range interactions may be such that intermediate phases with remarkable structural topologies, characterized by well-ordered patterns of HS and LS Fe\(^{II}\) molecular species, may be stabilized in a more or less wide temperature range, providing a two-step character. Commensurate intermediate superstructures\(^24\),\(^30\)–\(^36\),\(^40\)–\(^43\) or incommensurate metastable modulated structures\(^28\),\(^29\) may thus develop, most of which result from structural symmetry breaking transitions, coupled to the spin transition itself. These intermediate superstructures may be identified using detailed temperature-dependent x-ray structure analysis; the appearance of extra Bragg superstructure reflections on the x-ray diffraction pattern is a direct signature of the development of the additional long-range order. In some cases, short-range correlations provide only a partial ordering of the HS and LS Fe\(^{II}\) entities, as recently reported for the polymeric SCO material [Fe(NCSe)\(_2\))(bdpp)], for which a long-range HS-LS-HS-LS chain ordering with a complete disorder between adjacent chains has been evidenced by weak planes of diffuse scattering in the intermediate phase.\(^15\) The combination of

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interactions at the origin of a two-step transition is so subtle that a change of lattice solvate, or of counterion may be sufficient to severely affect the transition, or even completely suppress the two-step behavior.

A theoretical description of two-step transitions may be provided using Ising-like models or thermodynamic models based on one- or two-sublattice schemes. Two sublattices coupled antiferroelastically with intrasublattice ferroelastic based on one- or two-sublattice schemes. Two sublattices provided using Ising-like models or thermodynamic models of different Fe species, or degree of orientational disorder of a solvent lattice molecule) responsible for the long-range ordering of HS and LS molecular complexes. According to all these theoretical schemes, the two-step behavior originates from the close interplay between the SCO molecular system and the structural degrees of freedom, i.e., the molecular distortion and the lattice strain.

Detailed experimental insights into the photoexcitation and relaxation processes in two-step transition systems are still rather scarce. In common situations, the LIESST relaxation curve, defined as the evolution of $\gamma_{HS}$ as a function of temperature following photoexcitation, proceeds in a single step without passing through any intermediate phase. The corresponding isothermal relaxation curves, defined as the evolution of $\gamma_{HS}$ as a function of time in isothermal condition, exhibit single-exponential behaviors, with sometimes stretched elongated tails resulting from short-range correlations. In rare cases, a stepped LIESST relaxation or stepped isothermal relaxation curves have been reported and attributed to the successive relaxation of different Fe sites, although no crystallographic evidence has been provided. On the contrary, the possible stabilization of a long-range-ordered intermediate superstructure, resulting from a symmetry breaking scenario in the photoexcitation or relaxation regime, has never been reported. This is the fundamental question we address in the present study and clarify through time-dependent photocystallography.

The mononuclear Fe SCO compound [Fe(bapbpy)(NCS)$_2$] (I), where bapbpy = 6,6′-bis(aminom-2-pyridyl)-2,2′-bipyridine, undergoes a two-step thermal spin transition (Fig. 1), with both transition steps being first-order, and accompanied by reversible symmetry breaking crystallographic phase transitions and thermal hysteresis. The crystal structure has been reported at three temperatures (295 K, 190 K, and 110 K), which correspond to the three relevant states identified from the thermomagnetic behavior. In all three thermodynamically stable states, the crystal structure may be described as supramolecular chains of trans-[Fe(bapbpy)(NCS)$_2$] molecules connected through N-H...S hydrogen bonds and π-π stacking interactions running along the [001] crystallographic direction. Interchain interactions in the [110] and [110] directions are assisted by very weak C-H...S hydrogen bonds ($d_{H...S} > 2.9$ Å). State I (monoclinic $C2/c$) is observed above about 235 K and is characterized by a single HS Fe$^{II}$ center, located on a twofold rotation axis. Cooling below this temperature leads to state II (monoclinic $C2/c$), which is characterized by a tripling of the unit cell (a, b, c). A theoretical description of two-step transitions may be provided using Ising-like models or thermodynamic models based on one- or two-sublattice schemes. Two sublattices coupled antiferroelastically with intrasublattice ferroelastic based on one- or two-sublattice schemes. Two sublattices provided using Ising-like models or thermodynamic models of different Fe species, or degree of orientational disorder of a solvent lattice molecule) responsible for the long-range ordering of HS and LS molecular complexes. According to all these theoretical schemes, the two-step behavior originates from the close interplay between the SCO molecular system and the structural degrees of freedom, i.e., the molecular distortion and the lattice strain.

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II. CRYSTALLOGRAPHIC EXPERIMENTS

Five crystal structures, corresponding to different states with specific organizations of the molecular spin states, have
been determined under different procedures of temperature and/or time variation, and light irradiation conditions, as illustrated on Fig. 2. The structures are labeled IIQuench, III^LT, I^IIESST1, I^IIESST2, and III^Relax for the thermally quenched mixed spin state (10 K), relaxed LS state (15 K), photoinduced metastable HS state 1 (10 K), photoinduced metastable HS state 2 (15 K), and partially relaxed state after photoexcitation (15 K), respectively.

X-ray diffraction experiments were performed on single crystals using a Supernova 4-circle microsource diffractometer (Oxford Diffraction) equipped with a two-dimensional ATLAS charge-coupled-device (CCD) detector, and using Mo Kα radiation (λ = 0.71073 Å) for III^LT, I^IIESST1, and I^IIESST2. For IIQuench and III^Relax, Cu Kα radiation (λ = 1.54184 Å) was preferred in order to better separate superlattice reflections for these structural states with large unit cell volume. We used an Oxford Diffraction Helijet He open-flow cryosystem for cryogenic temperature measurements. For photoinduced experiments, an Ar-Kr gas laser coupled to a fiber optic (647 nm, 5mW) was used; the wavelength of the laser has been chosen after several irradiation tests and according to previously reported photomagnetic experiments. Data reduction was carried out using the CrvAlis software. The structures were solved by direct methods (SHELXS-97) and refined against F^2 by full-matrix least squares (SHELXL-97). Crystallographic details are provided in the Supplemental Material (Table S1). Selected bond lengths, angles, and additional structural parameters discussed in the text are summarized in Table I of this paper and in Tables S2, S3, and S4 of the Supplemental Material.

III. RESULTS

The structural analysis of SCO molecular crystals is very informative with respect to the spin transition process. The parameters of the Fe^{II} coordination sphere, such as bond lengths, angles, and octahedron volume V_p, are highly sensitive to the spin state; this is due to the redistribution of the valence electrons within the bonding and antibonding 3d orbitals of the central Fe^{II} cation upon spin-state change, as revealed from experimental electron density studies. A careful inspection of these parameters allows a clear assignment of the spin state for each Fe^{II} crystallographic site. Kinetic crystallographic measurements provide qualitative and quantitative insights on the phase transformation mechanisms associated with the spin-state change. The dynamics of like-spin-domain nucleation and growth for heterogeneous cooperative transitions has indeed been determined using kinetic thermo- and photocrystallographic techniques. In the following, we analyze successively the effect of a rapid quench cooling from room temperature to 10 K, the LS→HS photoexcitation process, and the subsequent HS→LS relaxation regime.

A. Trapping a metastable superstructure by quench cooling

At first, a single-crystal sample was rapidly quenched cooled from room temperature to 10 K, and a complete x-ray diffraction data set was collected at that temperature. The resulting diffraction pattern displays superstructure reflections in addition to the main Bragg reflections, which correspond to a commensurate modulation of the crystal structure with wave vector q = 1/3e^*, or equivalently a triple unit cell (a, b, 3c). For consistency with the structures already reported for the thermal transition by Bonnet et al., the structure IIQuench has been solved and refined in the C-centred cell ( monoclinic space group C2/c) with cell parameters a = 15.7695(7) Å, b = 10.6880(6) Å, c = 42.313(1) Å, β = 116.450(4)°. The I→IIQuench phase transition upon thermal quenching at 10 K may be described as a group-subgroup isomorphic transition, without changing the space group type (C2/c) but with a tripling of the unit cell volume. The overall crystal packing in the structure IIQuench remains similar to those derived for the thermodynamically stable state II obtained at 190 K during

<table>
<thead>
<tr>
<th>IIQuench</th>
<th>III^Relax</th>
<th>III^LT</th>
<th>I^IIESST1</th>
<th>I^IIESST2</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_9Fe1N6 (Å)</td>
<td>1.960(4)</td>
<td>1.958(8)</td>
<td>1.955(4)</td>
<td>2.147(1)</td>
</tr>
<tr>
<td>d_9Fe2N6 (Å)</td>
<td>2.138(4)</td>
<td>2.096(8)</td>
<td>2.096(8)</td>
<td>2.149(1)</td>
</tr>
<tr>
<td>Σ1 (deg)</td>
<td>57.36</td>
<td>57.00</td>
<td>57.13</td>
<td>99.93</td>
</tr>
<tr>
<td>Σ2 (deg)</td>
<td>94.00</td>
<td>83.60</td>
<td>99.77</td>
<td></td>
</tr>
<tr>
<td>V_p(Fe1N6) (Å^3)</td>
<td>9.91(4)</td>
<td>9.93(7)</td>
<td>9.83(4)</td>
<td>12.49(2)</td>
</tr>
<tr>
<td>V_p(Fe2N6) (Å^3)</td>
<td>12.40(4)</td>
<td>11.88(9)</td>
<td>12.53(1)</td>
<td></td>
</tr>
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</table>
the thermal study. The hydrogen bonds and $\pi-\pi$ interactions along the supramolecular [001] chains (Fig. S1 in the Supplemental Material) are barely significantly shorter than that characterized for state II (Tables S3 and S4). All the derived structural parameters (Table I, Table S2), especially the Fe-N bond distances $d(\text{Fe-N}) = 2.138(4)$ Å, $d(\text{Fe2-N}) = 2.138(4)$ Å, angular distortion parameters $\Sigma_1 = 57.36^\circ, \Sigma_2 = 94.00^\circ$, and FeN$_6$ octahedron volumes $V_p(\text{Fe1}) = 9.91(4)$ Å$^3, V_p(\text{Fe2}) = 12.40(4)$ Å$^3$ indicate that the asymmetric unit consists of one LS molecule on a general crystallographic position (Fe1) and half of a HS molecule sitting on a twofold axis (Fe2). The structure II$\text{Quench}$ presents therefore an ordered [HS-LS-LS] motif (see Fig. S1), very similar to the structural topology of the intermediate-state II previously described by Bonnet et al. in their temperature variation study. It is also isostructural with the intermediate state revealed at ambient temperature under hydrostatic pressure of 4.6 kbar.

The self-organization of the Fe$^{II}$ HS and LS molecules within the crystal lattice to form the [HS-LS-LS] motif is the origin of the commensurate modulation, and tripling of the unit cell in the crystallographic c direction. This process produces in parallel a lattice relaxation characterized by a harmonic displacive modulation of the structure with wave vector $q = 1/3c^*$ and transverse displacement along the direction [010]; the Fe$^{II}$ cations are displaced by as much as 0.608 Å from the regular $y = 0$ position (Figs. 3 and 4) (the displacement is only 0.110 Å in state I at room temperature). The Fe...Fe separation distances along the supramolecular [001] chains are also modulated, the HS...LS contacts being shorter by 0.108 Å with respect to the LS...LS contacts, corresponding to longitudinal displacements (Fig. 3). This commensurate modulation of the crystal structure II$\text{Quench}$ results from a delicate coupling between spin-state ordering and displacive distortion; this coupling is expected to be quite strong in such ferroelastic materials. Since the chains are related by cell translations in the a and b directions and by the C lattice centering, corresponding to the translation symmetries $t = a, t = b$ and $t = 1/2a + 1/2b$, respectively, the corrugation of adjacent chains in the packing is exactly in phase. As a consequence the modulation does not modify severely the nature and length of the weak interchain C-H...S contacts.

The trapping of a HS metastable phase at cryogenic temperature from rapid-quench-cooling a single-crystal sample is not uncommon for SCO materials. To prove effectively the metastability of the thermally quenched structural state II$\text{Quench}$ in I, the single-crystal sample was subsequently warmed to 60 K while monitoring the unit cell volume and presence of superstructure reflections; no significant evolution was detected up to 60 K (data not shown). At 60 K, the superstructure reflection rapidly disappeared jointly with a unit cell volume contraction. This is attributed to the relaxation from the metastable state II$\text{Quench}$ to the thermodynamically stable state III. This temperature of 60 K closely matches the 7/(LIESST) temperature derived from the photomagnetic measurements. Owing to the slow relaxation from state II to the thermodynamically stable state III in the tunnel relaxation regime at 10 K, we can therefore consider that the structure II$\text{Quench}$ corresponds to a metastable state II trapped at very low temperature.

The sample was then cooled from 60 K to 15 K, and a complete x-ray diffraction data set was collected. The corresponding crystal structure (labeled hereafter III$^{LT}$) was derived in the nonstandard space group C1, with cell parameters $a = 15.7351(11)$ Å, $b = 10.5753(7)$ Å, $c = 14.1454(11)$ Å, $\alpha = 93.975(6)^\circ, \beta = 116.113(7)^\circ, \gamma = 90.121(6)^\circ$. This structure is non-merohedrally twinned with the twin element being a twofold axis parallel to the crystallographic [010] direction of the C-centered cell, as reported previously for the structural analysis of state III at 110 K. With respect to the structure II$\text{Quench}$, the asymmetric unit of III$^{LT}$ contains only one
molecule located on a general position. The II\textsubscript{Quench} \rightarrow III\textsuperscript{ILIESST1} transition is therefore associated with a symmetry breaking process. The Fe-N bond lengths $[d_{\text{Fe}-\text{N}}] = 1.955(4)$ Å, iron coordination octahedron volume $[V_o = 9.83(4)$ Å$^3]$, and angular distortion parameter ($\Sigma = 57.13^\circ$) are typical for Fe$^{II}$ centers in the LS state (Table I) and comparable to those already reported for state III at 110 K.\textsuperscript{40} Upon the II\textsubscript{Quench} \rightarrow III\textsuperscript{ILIESST1} structural change, the commensurate modulation is lost, as revealed by the disappearance of the superstructure reflections. The displacement of the Fe$^{II}$ cations from the regular position $y = 0$ is reduced to 0.065 Å (Fig. 3). The supramolecular [010] chains consist of LS molecules with alternatively short and long contacts; the corresponding Fe...Fe separation distances are 6.9521(16) Å and 7.1967(16) Å.

B. Photoexcitation process and multimetastability

A fresh single-crystal sample was prepared beforehand in the II\textsubscript{Quench} state at 10 K by quench cooling as described in Sec. III A, and was subsequently irradiated with an Ar-Kr gas laser (647 nm, 5 mW). The crystal structure of the metastable light-induced state (labeled III\textsuperscript{ILIESST1}) was derived under permanent state.\textsuperscript{6} Upon the II\textsubscript{Quench} \rightarrow III\textsuperscript{ILIESST1} light-induced state change, the commensurate modulation is lost, as revealed by the complete disappearance of the superstructure reflections, and the unit cell volume decreases by a factor of 3. The resulting structure contains half a molecule in the asymmetric unit in the C2/c space group with cell parameters $a = 15.913(1)$ Å, $b = 10.8466(5)$ Å, $c = 14.1359(8)$ Å, $\beta = 117.211(8)^\circ$. The corresponding Fe-N coordination distances $[d_{\text{Fe}-\text{N}}] = 2.147(1)$ Å, FeN$_6$ octahedron volume $[V_o = 12.49(2)$ Å$^3]$, and angular distortion parameter ($\Sigma = 99.93^\circ$) indicate that the LS molecule of the state II\textsubscript{Quench} has been switched to the HS state. The displacive modulation is lost, and the displacement of the Fe$^{II}$ cations from the regular position $y = 0$ is reduced to 0.054 Å (Fig. 3). In parallel, the alternation of short Fe(LS)...Fe(HS) and long Fe(LS)...Fe(LS) contacts, which characterizes the structure II\textsubscript{Quench}, disappears in structure III\textsuperscript{ILIESST1}. All intramolecular and intermolecular structural parameters are very similar to those derived for state I at 295 K, taking into account thermal contraction effects.\textsuperscript{40} Those results confirm that the displacive modulation of the structure II\textsubscript{Quench} is intrinsically related to the [HS-LS-LS] spin state ordering.

Multimetastability is the ability to populate multiple metastable states with different physical (magnetic, optical, structural) properties. It has been observed for a very limited number of SCO complexes.\textsuperscript{28,29,36,69–71} In [Fe(bpp)$_2$](CF$_3$SO$_3$)$_2$·H$_2$O for instance, multimetastability manifests itself by two different relaxation mechanisms for the HS thermally trapped and LIIESST HS states. This is possibly related to an additional structural phase transition influencing the HS \rightarrow LS relaxation for the thermally trapped state.\textsuperscript{69} Multimetastability has also been shown to occur for some mononuclear and dinuclear spin-crossover complexes undergoing two-step spin transitions. For instance, the complex Fe(abp)$_2$(N[CN]$_2$)$_2$ exhibits two different metastable HS states at very low temperature, upon rapid thermal quenching from room temperature and upon light excitation from the LS state through the LIIESST effect.\textsuperscript{28,29} Both metastable states exhibit an incommensurate modulation of the crystal structure, with a distinct modulation wave vector: The two metastable states are structurally different without any ambiguity. The photocrystallographic investigation of the dinuclear complex [Fe(bt)(NCS)$_2$]$_2$(bpym) has proved that depending on the wavelength of the photoexcitation source (i.e., 1310 nm or 800 nm), different metastable states with HS-LS or HS-HS structural configuration may be selectively populated.\textsuperscript{70,71} As far as I is concerned, multimetastability is crystallographically demonstrated here since state II\textsubscript{Quench} and III\textsuperscript{ILIESST1}, which are observed under very different phase transformation pathways (Fig. 2), present very different structural architectures, characterized by an ordered [HS-LS-LS] motif for the former and a single HS site for the latter.

In order to explore the additional possibility of purely photoinduced multimetastability, we undertook a photoexcitation experiment on the crystal previously prepared in its thermodynamically stable LS state at 15 K, III\textsuperscript{ILIESST1}. The sample was irradiated with an Ar-Kr gas laser (647 nm, 5 mW); the crystal structure of the metastable light-induced state (labeled III\textsuperscript{ILIESST2}) was derived under permanent state.\textsuperscript{6} Those results confirm that the displacive modulation of the structure II\textsubscript{Quench} is intrinsically related to the [HS-LS-LS] spin state ordering.

C. Two-step relaxation

The photomagnetic measurements performed on a polycrystalline sample by Bonnet \textit{et al.} show “a singularity in the relaxation curve around 40 K, which might indicate a two-step relaxation process,” as shown in Fig. 1.\textsuperscript{41} The multimetastability demonstrated by the present crystallographic investigations (i.e., structures II\textsubscript{Quench}, III\textsuperscript{ILIESST1}, and III\textsuperscript{ILIESST2}) renders the hypothesis of a two-step relaxation indeed conceivable. To explore this possibility, we followed the evolution of the diffraction pattern after photoexcitation to the III\textsuperscript{ILIESST2} state.
in two ways: (i) while gradually raising the temperature from 10 K to 70 K (Fig. 5), and (ii) as a function of time in isothermal condition at 40 K (Fig. 6).

(i) While gradually increasing the temperature from 10 to 70 K in the I\textsubscript{LIESST2} state, no significant evolution of the unit cell volume is observed up to 40 K. At 50 K, the diffraction pattern suddenly displays superstructure reflections, related to the tripling of the unit cell parameters (a, b, 3c), while the unit cell volume per formula unit (V/Z) decreases to 534.7(5) ˚A\textsuperscript{3}. This value matches the unit cell volume per formula unit of the structure II\textsubscript{Quench} quite closely [V/Z = 532.1(1) ˚A\textsuperscript{3}]. After this initial drop, the unit cell volume is almost constant up to 60 K and then finally decreases to a value corresponding to state III. In parallel, the superstructure reflections disappear. This singularity in the evolution of the unit cell while increasing the temperature is in good agreement with the \(T_{LIESST}(\text{LIESST})\) value of 55 K, and demonstrates a two-step structural relaxation process, related to the transient stabilization of an intermediate structural state.

(ii) The relaxation process has also been investigated from the evolution of the unit cell parameters and diffraction pattern as a function of time in isothermal conditions at 40 K, allowing picturing a complete scenario of the structural phase transformation I\textsubscript{LIESST2} \(\rightarrow\) III; three consecutive stages may be identified (Fig. 6).

In the early step (within 50 min), a rapid and nonlinear decrease of the unit cell volume per formula unit occurs. Superstructure reflections, which can be indexed with the commensurate wave vector \(q = \frac{1}{3}c^*\), progressively develop, indicating the growth of a superstructure intermediate state (structure labeled II\textsubscript{Relax}). The sigmoidal trend of the unit cell evolution indicates that this state transformation takes place in a cooperative manner. As detailed in Fig. 7, the evolution of the unit cell parameters is anisotropic during this first period, the crystallographic \(b\) axis shortens progressively by about 1.7%, while the \(a\) and \(c\) axes decrease by 0.6% and 0.4% respectively, which is the reason for the unit cell volume contraction. The intensity profile along the [-3 5 1] row as a function of time (Fig. 8) clearly shows that the superstructure reflections may be detected around \(t = 37\) min [see reflection (-3 5 7) for instance]—that is to say, well after the contraction of the crystallographic \(b\) axis started. At this point, the intensity of the superstructure reflections is almost 1/3 of their intensity at the end of stage 1 (Fig. 9). The intensity of the (-3 5 6) reflection decreases almost to zero during the first step of the transformation (from \(t = 0\) to \(t = 50\) min), and as such, it may be taken as a signature of the disappearance of the state I\textsubscript{LIESST2}.

In the second step, the unit cell volume is constant over a period of 150 min, during which a large modification of the diffraction pattern occurs. It is noteworthy that the cell parameters do not change significantly during this period, with the exception of a gradual slight increase of the \(c\) axis. However, the diffraction pattern still evolves drastically (Fig. 6), as well as the intensity of some of the superstructure reflections, revealing that the phase transformation is still proceeding.
albeit at constant unit cell volume. From $t = 58$ min, the intensity of the reflection ($-3\ 5\ 7$) gradually decreases, which is a clear indication that a structural transformation is indeed developing on the plateau. We consider that twin domains are progressively formed throughout the crystal during this period. On the contrary, the ($-3\ 5\ 11$) reflection is completely insensitive to the twin formation as its intensity is not changing significantly after the first rapid increase to $t = 58$ min. At $t \approx 215$ min, the unit cell parameters $a$ and $b$, and to a lower extent $c$, present an abrupt decrease, and consequently the unit cell volume reduces, corresponding most probably to the final $\text{II}_\text{Relax} \rightarrow \text{III}$ phase transition.

One fundamental question is whether the intermediate modulated state $\text{II}_\text{Relax}$ observed during the isothermal relaxation at 40 K exhibits a superstructure with an ordered pattern of HS and LS species, similar to the structures II, $\text{II}_\text{Quench}$, and $\text{II}^{\text{II}}$. Unfortunately, the crystal structure of the modulated intermediate state $\text{II}_\text{Relax}$ could not be derived experimentally from the previous crystallographic measurement at 40 K. Indeed, thermal fluctuations are strong enough at this temperature to overcome the energy barrier to relaxation to the LS state, leading to a limited lifetime of the $\text{II}_\text{Relax}$ state at 40 K. According to the two-step isothermal relaxation was repeated at 40 K on a fresh crystal, monitoring carefully the evolution of the unit cell volume and appearance of the superstructure reflections as a function of time. Once the single-crystal sample reached the intermediate plateau, the temperature of the cryosystem was decreased rapidly to 15 K to decrease as much as possible the effect of thermal fluctuations, and thus increase sufficiently the lifetime of the $\text{II}_\text{Relax}$ state to enable a structural determination. A complete diffraction data collection was performed, and the corresponding crystal structure $\text{II}_\text{Relax}$ was derived. It is important to stress that this procedure is very delicate. Obviously, the quality of the corresponding diffraction data is lower than for all the other crystal structures we derived in the present work, since the crystal suffered significant damage owing to the sequence of phase transitions it underwent before reaching the final point at which the data collection was performed. Correlatively, the internal agreement factor of the data collection ($R_{int}$) and the agreement factors of the least-squares structural refinement ($R(F^2)$ and $wR(F^2)$) are significantly higher than for all the other crystal structures. However, we consider that this structural analysis is relevant and accurate enough for getting decisive structural information on the relaxation mechanism. As given in Table I (and Table S2), the coordination environment of Fe1 in state $\text{II}_\text{Relax}$ is very similar to those derived for Fe1 in state $\text{II}_\text{Quench}$, while Fe2 exhibits average Fe-N coordination distances, $\Sigma$ angular distortion parameter, and FeN$_6$ octahedron volume close to but slightly lower than those expected for a genuine HS Fe$^{II}$ environment. This may be attributed to the difficulty in efficiently trapping the crystal in the $\text{II}_\text{Relax}$ state using our experimental procedure. It is therefore convincing that the $\text{II}_\text{Relax}$ crystal structure exhibits the same [HS-LS-LS] superstructure as in all other stable or metastable structures of state II. The transverse displacements of the two Fe$^{II}$ cations from the regular $y = 0$ position amounts to 0.318 Å and 0.564 Å for Fe1 and Fe2, respectively, under the effect of the displacive modulation concomitant with the [HS-LS-LS] spin state ordering. These values are close to those derived for the structure $\text{II}_\text{Quench}$, which gives strong evidence that the step in the relaxation process is related to the stabilization of an ordered [HS-LS-LS] superstructure.

IV. DISCUSSION

We have shown through our crystallographic analysis that the LIESST relaxation in I occurs in two successive steps with an intermediate plateau, which manifests itself in the relaxation while raising the temperature, and as a function of time in isothermal condition. This is an outstanding behavior that deserves additional comments. The two-step relaxation involves the sequence of states $\text{IIESST} \rightarrow \text{II}_\text{Relax} \rightarrow \text{III}$. The first step of the transformation is associated with the development
of a commensurate modulated superstructure, during which the unit cell triples (a, b, c) and the point group symmetry 2/m is preserved. It may be described as a group-subgroup isomorphic transition, without changing the space group type (C2/c). The stabilization of the intermediate superstructure state reveals a structural instability originating from a strong coupling between lattice distortions (spontaneous strain) and molecular spin state change. It leads to a displacive modulation of the structure with wave vector \( \mathbf{q} = 1/3 \mathbf{e}^a \) and large displacement amplitudes (up to 0.564 Å). The second step is associated with a symmetry breaking from state \( \Pi_{\text{Relax}} \) to the lower symmetry structure of state III, the twofold axis is lost, the point group symmetry decreases to \(-1\), and the unit cell volume is divided by 3. Accordingly, the sequence of phase transition \( \Pi_{\text{LIESST}} \rightarrow \Pi_{\text{Relax}} \rightarrow \Pi_{\text{III}} \) does not belong to the reentrant situation. The two steps of the transformation generate large elastic strain, which has also been observed during the thermal transition by polarized light measurements.\(^{55}\) Especially during the second step \( \Pi_{\text{Relax}} \rightarrow \Pi_{\text{III}} \), the crystal lattice distorts appreciably as reflected by the deviation of the angle \( \alpha (\alpha \approx 94°) \) from the monoclinic value \( (\alpha = 90°) \), while the angle \( \gamma \) does not deviate so strongly \([\gamma = 90.1216(6)°]\). In order to accommodate the corresponding change in structure and the associated strain, the crystal adopts a collective response and tends to develop transformation twins. The twofold symmetry axis which is lost during the symmetry breaking transition relates the individual twin components; the associated composition plane is the (ab) plane of the triclinic crystal (Fig. S2). This is consistent with the optical microscopy observations during the thermal transition \( \Pi_{\text{II}} \rightarrow \Pi_{\text{III}} \), which revealed a homogeneous domain pattern characterized by micrometric stripes with domain walls of parallel orientations (lamellar twin) parallel to the crystallographic c axis.\(^{55}\) This is a quite common twin domain pattern for ferroelastic materials.\(^{72}\) The twin formation results in a close-to-zero net spontaneous strain as a result of mutual cancellation; the elastic energy has to be minimized on a mesoscopic scale; this is the driving force for the twin formation.\(^{72}\)

Two-step relaxation following LIESST is very uncommon in SCO materials. It has been reported for just a few systems,\(^{16,17,36,38,39,43}\) but it has never been characterized and successfully interpreted on the basis of the underlying evolution of the crystal structure. The most trivial situation is that of several crystallographic Fe\(^{II}\) sites in the metastable HS state, in which case the several steps of the relaxation are associated with the successive, and not concomitant, relaxation of the different sites owing to different lifetime of the metastable HS molecular species. For [Fe(DPEA)(bim)][ClO\(_4\)]\(_2\)-0.5H\(_2\)O, two LIESST relaxation temperatures have been detected in the \( \frac{\partial (\chi_M T)}{\partial T} \) versus \( T \) plot by photomagnetic measurements (viz., 21 K and 36 K) and assigned to the two Fe\(^{II}\) sites having different \( \Pi_{\text{LIESST}} \) values.\(^{38}\) The same situation holds for [Fe(picpzpz)\(_2\)][BF\(_4\)]\(_2\)-MeOH with the two relaxation temperatures being 49 K and 70 K.\(^{39}\) On the contrary, the isothermal relaxation at 10 K for this former compound did not evidence any two-step character, but rather a stretched exponential behavior, which has been well adjusted to a biexponential relaxation law. The same situation has been reported for the fascinating SCO material Fe(dpdpz)\(_2\)[Ni(mnt)]\(_2\)-MeOH, whose thermal spin transition exhibits three intermediate states. One of these states (labeled state IM1 in Ref. 36) corresponds to a superstructure in a tripled unit cell with 1/3 Fe\(^{II}\) in the HS state and 2/3 Fe\(^{II}\) in the LS state. Interestingly, the magnetic and photomagnetic measurements indicate that the trapped HS state relaxes to the LS state in two steps with a \( \chi_M T \) value at the intermediate plateau which is close to those of the IM1 state. This suggests that the two-step relaxation proceeds through the intermediate IM1 state, although no crystallographic results have been provided by the authors to confirm this important issue. The HS→LS relaxation kinetics of the SCO coordination polymer Fe(pmd)[Ag(CN)\(_2\)]\(_2\)[Ag\(_2\)(CN)\(_3\)] has been investigated in detail by optical spectroscopy as a function of temperature between 15 and 55 K.\(^{17}\) The derived isothermal relaxation takes place via a two-step cooperative process, which has been attributed to the successive individual relaxation of the five independent Fe\(^{II}\) sites. The two-site (or two groups of sites) explanation for those two-step relaxations is relevant since it is well known that \( T_{\text{LIESST}} \) is primarily governed by the geometry of the inner coordination sphere and conformational rigidity of the coordinating ligands, while the intermolecular interactions in the crystal packing are supposed to have a minor influence.\(^5\) However, in several other SCO systems with two-step thermal transitions, LIESST relaxation proceeds in a single step without passing through any intermediate state.\(^{10,31,37,42}\) In such cases, one single \( T_{\text{LIESST}} \) relaxation temperature is characterized, while the relaxation kinetics can be adequately described by a single sigmoidal law or a stretched exponential. The SCO mononuclear system [Fe(pic)\(_3\)]Cl\(_2\)-EtOH is the most well known representative example of these. It exhibits a two-step thermal spin transition coupled to a symmetry breaking phenomenon which leads to an ordered superstructure on the plateau.\(^{35}\) The HS→LS relaxation following LIESST at cryogenic temperature exhibits the typical sigmoidal behavior with stretched elongated tails resulting from short-range correlations.\(^{10}\) The two-site explanation for a two-step relaxation does not hold for I since the crystal structure of the \( I_{\text{LIESST}} \) and \( I_{\text{LIESST}} \) states evidences only one symmetrically independent HS site. On the contrary, the crystallographic analysis reveals that the HS→LS relaxation is associated with a double symmetry breaking phenomenon with the stabilization of an intermediate superstructure state \( \Pi_{\text{Relax}} \). To the best of our knowledge, I is the first example of a SCO compound exhibiting such a two-step relaxation process that has been elucidated crystallographically.

In the dynamic regime, two-step relaxations may well be interpreted on the basis of Ising-like models with antagonistic interactions between two coupled sublattices,\(^{48,50,73,74}\) or alternatively considering antiferroelastic short-range interactions balanced by ferroelastic long-range interactions without introducing two sublattices.\(^{10}\) In all these schemes, the intermediate state results from an instability originating from the competing interactions or competing sublattices, leading in some cases to an ordered pattern of HS and LS species (i.e., a superstructure).\(^{74}\) Two regimes in the relaxation curves may emerge for strong enough antiferroelastic intersublattice interactions.\(^{73}\) It is noteworthy that these interactions control the width of the plateau at the two-step thermal transition as well; the width has been shown to depend linearly on the value of the intersublattice coupling constant.\(^{48,73}\) As shown
Two-step thermal transition with a HS to LS population ratio occur as a function of temperature. As far as or 1 step relaxations with trapping to the intermediate state can lifetime of the HS and intermediate states, so that 1 step, 2 step, intersublattice plays a fundamental role in the metastability and exception being the I $\rightarrow$ II light-induced transition. This is noteworthy that some of the transformation pathways are reversible, while some are completely irreversible (I $\rightarrow$ II$^{\text{Quench}}$ for instance). It is also remarkable that the superstructure has been probed by rapid thermal quenching and structurally characterized at 40 K, that is to say, close to T(LIESST). Such a two-step relaxation associated with a symmetry breaking transition has been predicted to occur for strong intersublattice interactions while raising the temperature under continuous light irradiation in the so-called LITH regime (light-induced thermal hysteresis), i.e., close to T(LIESST).

Figure 2 summarizes all the states of I that have been structurally characterized from crystallography as a function of temperature, pressure, and light irradiation. It also shows the transformation pathways relating these states. It is noteworthy that some of the transformation pathways are reversible, while some are completely irreversible (I $\rightarrow$ II$^{\text{Quench}}$ for instance). It is also remarkable that the superstructure with ordered [HS-LS-LS] motif is involved as an intermediate state in almost all the I$\rightarrow$III phase transformations, the only exception being the I$\rightarrow$III light-induced transition. This is not surprising since photoexcitation is intrinsically a random process, which breaks short-range correlations. The build-up of such correlations would be crucial for the development of an ordered intermediate superstructure. Photoexcitation curves reporting the evolution of the HS fraction $\gamma_{HS}$ as a function of time at very low temperature under continuous laser light irradiation are only rarely reported, and do not exhibit 2-step photoexcitation in general. As predicted by Parreira et al., a two-step photoinduced transition passing through a symmetry breaking intermediate state may occur in the LITH regime.

V. CONCLUSION

In summary, the light-induced excitation and subsequent relaxation regime at cryogenic temperature of the two-step SCO complex [Fe(bapby)(NCS)$_2$] have been investigated by time-dependent photocrystallography. Upon photoexcitation from the totally LS phase (structure III$^1$), a direct population of the totally HS phase (structure I(LIESST$^2$) occurs, without involving any intermediate structural phase. The relaxation from the metastable state I(LIESST$^2$) at 40 K proceeds in two steps. The first step corresponds to the cooperative transformation to an intermediate superstructure II$^{\text{Relax}}$ characterized by a long-range-ordered [HS-LS-LS] motif coupled to a commensurate displace modulation. In a second stage, state II$^{\text{Relax}}$ undergoes a transformation twinning towards the LS state III, triggered by lattice strain. The formation of the superstructure is driven by strong molecule-lattice coupling, and results from the subtle interplay between short-range interactions and ferroelastic long-range interactions along the supramolecular chains. The long-range-ordered [HS-LS-LS] superstructure has also been trapped as II$^{\text{Quench}}$ by rapid thermal quenching of state I to cryogenic temperature. I exhibits therefore multimetastability (states I(LIESST$^1$, I(LIESST$^2$, II$^{\text{Relax}}$, II$^{\text{Quench}}$), which has been completely characterized structurally. This property of multimetastability is of the utmost importance, paving the way for the development of innovative multiswitchable molecular systems. To the best of our knowledge, I is the first example of a SCO compound exhibiting such a two-step relaxation related to a double symmetry breaking process to have been elucidated crystallographically.

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MULTIMETASTABILITY, PHOTOTRAPPING, AND . . .


67The angular distortion parameter $\Sigma$ is defined as the sum of the absolute values of the deviation from 90°, of the 12 cis angles in the coordination sphere.


