Aperiodic Spin State Ordering of Bistable Molecules and Its Photoinduced Erasing

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(Received 26 July 2012; published 21 December 2012)

We describe a novel type of ordering phenomenon associated with the incommensurate occupational modulation of bistable molecular magnetic state in a spin-crossover material. This unusual type of aperiodicity resulting from the ordering of multistable electronic states opens new possibilities for addressing such materials by light. Here we show that light can switch the crystal from four- to three-dimensional periodic structure. Mixing aperiodicity, multistability, and photoinduced phenomenà opens new perspectives for directing complex order and function in material science.

DOI: 10.1103/PhysRevLett.109.257206 PACS numbers: 75.30.Wx, 61.44.Fw, 64.70.Rh, 82.50.Hp

The control of the functionality of a material requires understanding the complex organization of its atomic or electronic constituents, but also understanding the bistable or multistable processes addressable by external stimulation, including light for the photocontrol [1–4]. On the one hand, macroscopic ordering is manifested by the appearance of regular patterns, which in some cases never repeat themselves periodically in three-dimensional (3D) space but only in a higher dimension space: this so-called aperiodicity [5–7] plays a central role in the structure and physical properties of materials as diverse as quasicrystals [8], charge-density [1], and spin-density waves [9,10], or new superconductors [11], for instance. On the other hand, some materials exhibit more or less cooperative switching between bistable functional molecular states [12–15], controllable with, for example, temperature, pressure, and light. The relationship between molecular bistability in the solid state and aperiodicity has not been considered so far. Here, we describe a novel type of ordering phenomenon associated with the appearance of an incommensurate molecular spin state modulation of a bistable spin-crossover compound. It results from a concerted interplay between the symmetry breaking associated with the aperiodic ordering and the thermal balance between the two functional states. Contrary to usual incommensurate composition systems [16–19], for which the species concentrations are chemically fixed, in bistable systems the average concentration of molecular states can fluctuate, evolve, and be controlled by external stimuli. And so we show that a laser excitation, selectively populating a single molecular state, can erase the incommensurate phase and switch the crystal structure from four-dimensional (4D) to 3D periodic. Mixing aperiodicity, multistability, and photoinduced phenomena opens new perspectives for directing complex order and function.

Fe(II)-based spin-crossover (SC) compounds are prototypic bistable molecular systems. Both basic scientific research [20] and potential technological applications were investigated because of ultrafast switching [21], information storage, or visual display [13,22] abilities. The possibility offered by various external control parameters such as temperature, pressure, or light irradiation for balancing the relative population between low-spin (LS, $S = 0$) and high-spin (HS, $S = 2$) states has attracted much interest and many such complexes have been widely studied over the past decades [12]. In addition to simple entropy-driven macroscopic conversion from LS to HS, complex phenomena resulting from the partial spin conversion and the periodic ordering of HS and LS states around stepped transitions have been described [23–26]. In this Letter we describe a novel type of phase, where the long-range order of HS and LS molecular states is incommensurately modulated with respect to the 3D structure. This exotic phase is observed in the new spin-crossover material $[Fe^{II}H_2L^{2\text{-}Me}][SbF_6]_2$ ($H_2L^{2\text{-}Me}$ denotes the organic ligand bis[((2-methylimidazol-4-yl)methylidene)-3-aminopropyl] ethylenediamine) [27]. We first describe the features of this novel modulated structure as obtained from a structure analysis in 4D superspace, and then we show that it can be erased by laser irradiation.

The $[Fe^{II}H_2L^{2\text{-}Me}]^{2+}$ cation in complexes is able to switch from HS to LS states when temperature is decreased as demonstrated in salts with $PF_6{}^-$ or $AsF_6{}^-$ anions [25,26,28]. The concentration in HS molecules (γ_{HS}) can be accurately measured by different techniques [12]: here we use magnetic susceptibility, Mössbauer spectroscopy, and x-ray diffraction to study the SbF_6^- complex. Figure 1 shows the temperature dependence of γ_{HS} estimated from the $\chi_M T$ product (Fig. S1), Mössbauer analysis (Fig. S2 and Table S1), and structure analysis by x-ray diffraction (Tables S2 and S3). In this family of complexes, the Fe(II) ion is coordinated by six nitrogen atoms of the ligand, in a nearly octahedral field [29]. It is well known that the change of d^6 shell occupancy between LS ($t_{2g}{}^6 - e_g{}^0$) and HS ($t_{2g}{}^4 - e_g{}^2$) is associated with an elongation of the average ⟨Fe-N⟩ bond length [23,24]. For [$Fe^{II}H_2L^{2\text{-}Me}$] cation in the PF_6 and AsF_6 salts, ⟨Fe-N⟩ changes from 2.01 Å (LS) to 2.19 Å (HS) [25,26,28]. At room temperature these complexes are isostructural to the reported SbF_6 derivative (space group $P22_12_1$; Fig. S3). When LS and HS states coexist in the crystal, structural analysis allows determining γ_{HS} through its correlation with ⟨Fe-N⟩, as this one is modified by the relative contribution of LS and HS states (Table S3) [25–27]. Figure 1 shows that above 230 K $\gamma_{HS} = 1$, whereas at low temperature, below 90 K, a plateau is reached at $\gamma_{HS} \approx 0.5$. This is characterized by the partial apparent contraction of ⟨Fe-N⟩ (2.10 Å; Table S3), the magnetic susceptibility (Fig. S1), and Mössbauer spectra (Fig. S2). The above-mentioned methods confirm the known agreement of structural analysis based on ⟨Fe-N⟩ for determining γ_{HS}, which we use to analyze the aperiodic structure.

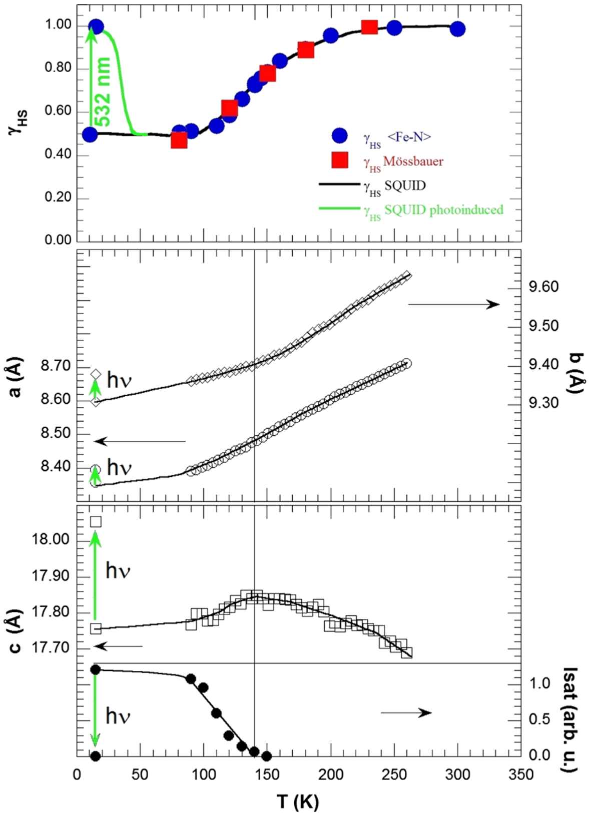

FIG. 1 (color online). Temperature dependence of the HS fraction γ_{HS} in the [$Fe^{II}H_2L^{2\text{-}Me}$][$SbF_6$]$_2$ complex, extracted from ⟨Fe-N⟩ bond length obtained by x-ray diffraction (filled circle), Mössbauer data (filled square), and magnetic susceptibility (lines) [27]. Photoinduced spin-state switching is performed at low temperature with 532 nm irradiation. The temperature dependence of the unit cell parameters **a** (open circle), **b** (open diamond), and **c** (open square) and of the average intensity (filled circle) of a few selected satellite reflections indicate a second order transition toward the incommensurate phase around 140 K and a photoinduced transition reached by irradiation at 532 nm ($h\nu$) at low temperature.

X-ray data collected below 150 K revealed new Bragg reflections (Figs. 2, S4, and S5) corresponding to a lowering of symmetry. On the one hand, Bragg reflections characterizing the loss of 2_1 screw axes along **b** and **c** (Fig. S6) indicate a change of the crystalline system from orthorhombic to monoclinic (**a** being the monoclinic axis). On the other hand, other types of numerous weak reflections appear, but cannot be indexed with three basis vectors. As shown in Figs. 2 and S4, a four-vector basis $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, and $\mathbf{q}$ must be used. However, because of the

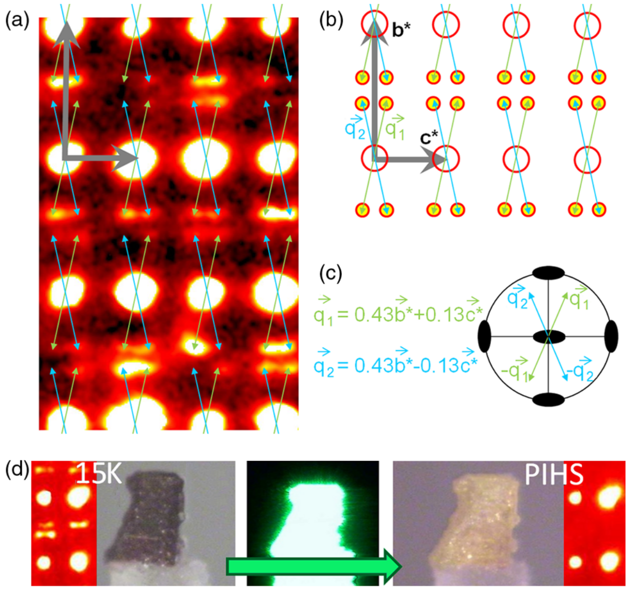

FIG. 2 (color online). Satellites' reflections in the aperiodic phase: (a) diffracted intensity in the ($\mathbf{b}^*$, $\mathbf{c}^*$) reciprocal plane, with intense Bragg reflections at the nodes and weak satellites' reflections in incommensurate positions observed in the aperiodic phase. (b) Schematic indexation of the reflections with ($\mathbf{b}^*$, $\mathbf{c}^*$, $\mathbf{q_1}$) or ($\mathbf{b}^*$, $\mathbf{c}^*$, $\mathbf{q_2}$). (c) Stereographic projection along a of the four branches star of **k** in the 222 symmetry class (twofold axes are represented by solid ellipses): two types of domains exist, each associated with a modulation vector $\mathbf{q_1}$ or $\mathbf{q_2}$. Any reflection is therefore indexed $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}_1$ or $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q_2}$. (d) At 15 K in the incommensurate phase with satellite reflections the crystal color is dark purple. In the photoinduced HS state reached after photoexcitation at 532 nm the crystal color is yellow, and the satellites reflections disappear, as in the HS state above 250 K.

symmetry lowering, two types of domains are formed in the star of **k** [Fig. 2(c)] corresponding to $\mathbf{q}_1$ or $\mathbf{q}_2$ (two directions equivalent in the high-symmetry phase). All these reflections are therefore indexed with the scattering vectors **Q** given by $\mathbf{Q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}_1$ or $\mathbf{Q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}_2$, h, k, l, and m being integers.

The two modulation vectors correspond to $\mathbf{q}_1 = \beta\mathbf{b}^* + \gamma\mathbf{c}^*$ and $\mathbf{q}_2 = -\beta\mathbf{b}^* + \gamma\mathbf{c}^*$. Since we found that $\beta = 0.431(5)$ and $\gamma = 0.131(5)$ (Fig. S4), the components of **q** are not simple fractional numbers, and thus the structure is incommensurately modulated [5–7]. Only main reflections ($m = 0$) and first-order satellites ($m = \pm 1$) are observed down to 15 K (Figs. 2 and S4). Reflections indexed by a combination $\mathbf{q}_1 \pm \mathbf{q}_2$ are not observed since the modulated structure is multidomain single **q** and the direction of the modulation vector corresponds to the decrease in symmetry from orthorhombic to monoclinic. Consequently, during this phase transition the symmetry changes from an orthorhombic ($P22_12_1$) system with 3D periodic structure to an incommensurately modulated structure with a 4D superspace group symmetry $P211(0\beta\gamma)$. The continuous evolution of the satellite reflections around 140 K, concomitant with a change of slope in the temperature dependence of the lattice parameters (Fig. 1), underline the second order nature of the phase transition.

The structure of the incommensurate phase was refined in a (3 + 1)-dimensional superspace [6]. The detailed description of the structural analysis is given in the supplemental material [27], and we focus here on the main conclusions. The aperiodic structure can be interpreted as resulting from a spatial modulation of the HS fraction, i.e., of the spin state of the molecules, simply written as

$$\gamma_{\mathrm{HS}}(\mathbf{r}) = \gamma_{\mathrm{HS}} + \eta \times \cos(\mathbf{q}\cdot\mathbf{r}),$$

where γ_{HS} is the average HS fraction determined in Fig. 1, **q** is the wave vector, and η is the amplitude of the wave. In several SC systems, superstructure ordering of γ_{HS} over crystalline sites were reported [23,25], including the isostructural PF_6 derivative [26]. For the latter, the spin-state ordering around an average value of $\gamma_{\mathrm{HS}} = 0.5$ corresponds to a cell doubling along the **c** axis, since $\mathbf{q} = \mathbf{c}^*/2$. Figure 3(a) depicts $\gamma_{\mathrm{HS}}(\mathbf{r})$, where sites are mainly HS (red) when $\gamma_{\mathrm{HS}}(\mathbf{r})$ is above 0.5, or mainly LS (blue) below. We extend this description to the present compound, for which the wavelength of the modulation of $\gamma_{\mathrm{HS}}(\mathbf{r})$ around $\gamma_{\mathrm{HS}} = 0.5$ is incommensurate with the average 3D lattice [Fig. 3(b)]. The sequence of HS and LS sites therefore never repeats periodically in the 3D space.

In the full structure model of a modulated structure [20], the atoms must be described by their positions in the average 3D unit cell and by their modulation functions along the fourth dimension coordinate x_4 of the superspace. From the refined superspace structure model, the modulation of $\langle Fe\text{-}N\rangle$ along x_4 can be obtained (Figs. S6 and S7), from which we estimate the amplitude of the modulation to $\eta \approx 0.37(5)$ (Fig. 4). The incommensurate spin-state occupation structure can be visualized in the (**b**, **c**) plane in Fig. 4, by using the same color code as in Fig. 3. Clearly, the main character of the modulation is the presence of stripes of HS and LS molecular states, perpendicular to the direction of the modulation vector **q**.

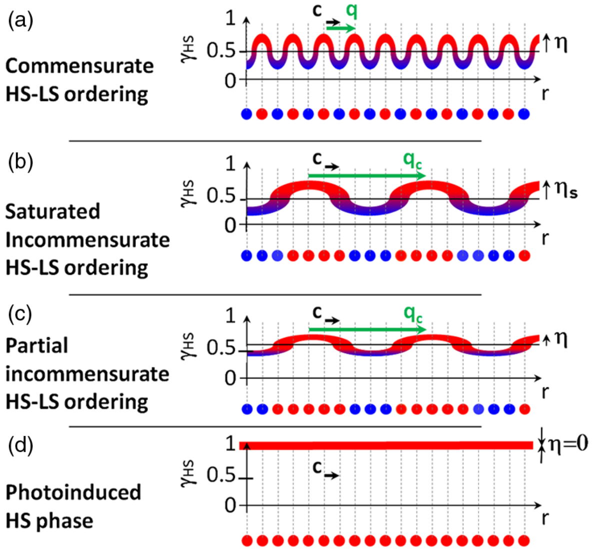

FIG. 3 (color online). HS-LS ordering schematically represented by an occupational wave $\gamma_{\mathrm{HS}}(\mathbf{r}) = \gamma_{\mathrm{HS}} + \eta \times \cos(\mathbf{q}\cdot\mathbf{r})$. (a) commensurate case ($\mathbf{q} = \mathbf{c}^*/2$) where the periodicity of the modulation is 2**c** (green) around an average value $\gamma_{\mathrm{HS}} = 0.5$ (line) and with an amplitude η, giving rise to alternation of mainly HS (red) and LS (blue) spin-state occupation over the different molecular sites (spheres) along the **c** axis. (b) Incommensurate case projected along the **c** direction ($\mathbf{q_c} = 0.131\mathbf{c}^*$) gives an aperiodic alternation around an average value $\gamma_{\mathrm{HS}} = 0.5$ and with a saturated amplitude η_s. (c) Intermediate incommensurate case characterized by a larger fraction of HS (red) sites with $\gamma_{\mathrm{HS}} > 0.5$ and an amplitude $0 < \eta < \eta_s$. (d) The photoinduced HS phase where $\gamma_{\mathrm{HS}}(r) = 1$ and the amplitude η of the concentration wave vanishes.

The possibility to control the average concentration of HS molecules by external parameter is an important new aspect with regard to usual incommensurate composition-type systems reported in the literature [5–7,16–19]. For these, the modulation vector can change when the amplitude of the order parameter η evolves with temperature, but the species concentration is chemically fixed. In the present system both the average concentration γ_{HS} and the amplitude η change with temperature but without significant variation of the modulation vector detected. From the temperature dependence of the intensity (Fig. 1) of satellite reflections (in a first approximation $\propto \eta^2$), we can conclude that, below 80 K, η saturates (around $\eta_s = 0.37$). These reflections disappearing around 140 K, the amplitude of occupation modulation wave vanishes ($\eta = 0$) when $\gamma_{\mathrm{HS}} \approx 0.75$, i.e., well before 230 K where $\gamma_{\mathrm{HS}} = 1$. An intermediate case corresponding to the 80–140 K range is illustrated in Fig. 3(c), where $\gamma_{\mathrm{HS}} > 0.5$ and $0 < \eta < \eta_s$.

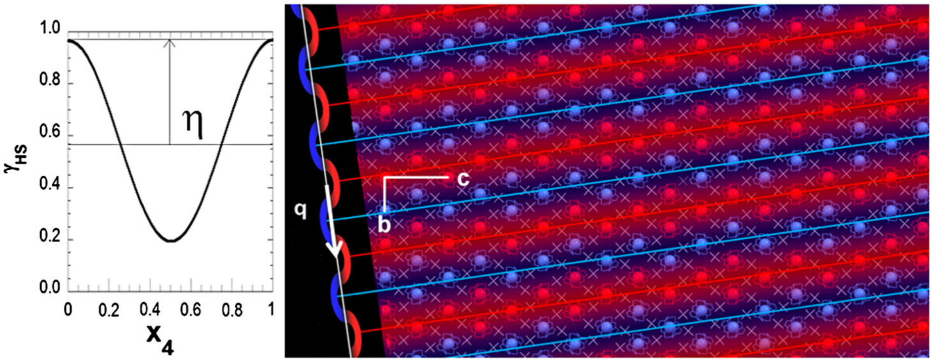

FIG. 4 (color online). The aperiodic spin state ordering with the modulation of γ_{HS} along the superspace coordinate x_4 (left), varying between 0.19(5) and 0.94(5), deduced from the modulation of the ⟨Fe-N⟩ bond in 4D space (Fig. S7). The corresponding structure is projected in 3D space: blue (LS states) and red (HS states) colors schematically reflect the spatial occupation modulation (right). The **b** and **c** crystalline axes of the average 3D structure are indicated.

These data clearly indicate different evolutions of γ_{HS} and η. The appearance of incommensurate structures results from competing interactions over different ranges. In the present case we can mention the competition between long-range elastic interactions and steric effects between the anion and cation layers (Fig. 4), also underlined in the AsF_6 derivative [25] for explaining complex but commensurate spin-states order.

Light is known to be an efficient control parameter in the prototype photoactive SC materials [12,20–22,30], and it was shown for $[Fe^{II}H_2L^{2\text{-}Me}]^{2+}$ that weak laser irradiation at 532 nm can promote the molecules from LS to HS [25,26,28]. Figure 1 shows that after a few minutes of irradiation at 15 K, $\gamma_{HS} = 1$, as characterized by the values of $\chi_M T$ and ⟨Fe-N⟩(2.19 Å). This photomagnetic effect is also related here to an important photochromic effect, since the crystal color changes from dark purple in the incommensurate low temperature phase to yellow in the photoinduced HS and thermal HS phases (Fig. 2), where the satellite reflections disappear. The structure of the photoinduced phase is again 3D periodic, and the disappearance of (0 k 0) and (0 0 l) Bragg reflections with k and l odd shows that the photoinduced phase recovers the orthorhombic $P22_12_1$ symmetry. Except for the thermal contraction of the lattice parameters (Fig. 1), the structures of the photoinduced HS and thermal HS phases are identical (Tables S2 and S3). This metastable photoinduced HS state has a lifetime longer than 24 h at 15 K once laser excitation is stopped. However, when warmed above 40 K, γ_{HS} relaxes back to ≈ 0.5 within a few minutes (Fig. 1) and the incommensurate phase is recovered. This behavior is proof that it is indeed the spin state that is the primary modulated parameter. When $\gamma_{HS} = 1$, the spatial modulation of $\gamma_{HS}(\mathbf{r})$ vanishes [$\eta = 0$, Fig. 3(d)] as only the HS state is occupied over all the crystalline sites.

Our detailed study of the $[Fe^{II}H_2L^{2\text{-}Me}][SbF_6]_2$ material shows that the incomplete conversion of bistable molecules is associated with an incommensurate spatial modulation of the molecular spin state and a description of the structure is obtained in (3 + 1)-dimensional superspace. The particularity of the present material is that, unlike conventional modulated crystals with occupational, positional, or conformational modulation, the primary modulated parameter is the spin state of bistable molecules. As such, this aperiodic structure is demonstrated to be erased by selective laser population of a single molecular state (HS).

With the development of scientific instrumentation, it appears that aperiodicity is ubiquitous in all types of materials. It is therefore very likely that the present concept of aperiodic ordering of molecular states may be applied to other types of photoactive materials exhibiting molecular bistability or multistability. By crossing the borders between aperiodicity, multistability, and photoinduced phenomena, we have shown that new perspectives appear for switching between different regimes of periodicity and for exploring new phases of matter related to function, such as photochromism and photomagnetism.

This work was supported by the Institut Universitaire de France, Rennes Métropole, Région Bretagne (CREATE Ultimate 4146), the ANR (09-BLAN-0212), and Europe (FEDER). H. W. thanks University Rennes 1 for PD funding. L. R. thanks CNRS for Ph.D. funding.

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