Velocity of the High-Spin Low-Spin Interface Inside the Thermal Hysteresis Loop of a Spin-Crossover Crystal, via Photothermal Control of the Interface Motion

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We investigated by optical microscopy the thermal transition of the spin-crossover dinuclear iron(II) compound [{Fe(NCSe)(py)$_2$}$_2$(m-bpypz)]. In a high-quality crystal the high-spin (HS) low-spin (LS) thermal transition took place with a sizable hysteresis, at ∼108 K and ∼116 K on cooling and heating, respectively, through the growth of a single macroscopic domain with a straight LS and HS interface. The interface orientation was almost constant and its propagation velocity was close to ∼6 and 26 μm s^{-1} for the on-cooling and on-heating processes, respectively. We found that the motion of the interface was sensitive to the intensity of the irradiation beam of the microscope, through a photothermal effect. By fine-tuning the intensity we could stop and even reverse the interface motion. This way we stabilized a biphasic state of the crystal, and we followed the spontaneous motion of the interface at different temperatures inside the thermal hysteresis loop. This experiment gives access for the first time to an accurate determination of the equilibrium temperature in the case of thermal hysteresis—which was not accessible by the usual quasistatic investigations. The temperature dependence of the propagation velocity inside the hysteretic interval was revealed to be highly nonlinear, and it was quantitatively reproduced by a dynamical mean-field theory, which made possible an estimate of the macroscopic energy barrier.

Switchable molecular solids such as spin transition (ST) compounds [1] are fascinating objects for physicists, since they display first-order phase transitions under the effects of various command parameters, such as temperature, light, pressure, magnetic field and—more recently—electric field [2]. They also are promising for various applications, such as photocontrolled pigments or drug vectors [3], photoluminescent microsensors [4], and current research aims to realize novel multifunctionalities for spintronics [5]. A few years ago the observation of ST single crystals by optical microscopy [6–9] was developed for investigating the spatiotemporal properties of the thermal spin transition. The results agree with the earlier investigations of molecular crystals [10,11], which revealed the universal mechanism of nucleation and growth. Optical microscopy is particularly appealing in the case of spin-crossover crystals because of their thermochromic and photochromic properties that are due to the presence of specific absorption bands (*d-d* transitions, metal-to-ligand charge transfer bands, etc.) at different wavelengths in the HS and LS states. In a recent work we introduced the concept of a multiscale stress-driven process for the thermal spin transition [9]. The continuous recording of the high-spin fraction (n_{HS}) maps, obtained by image processing, permits monitoring the propagation of the physical conditions (temperature and mechanical stresses, for instance) suitable for the nucleation and growth process. The frontline between the HS and LS

macroscopic domains can be abbreviated as ''HS and LS interface,'' actually, the ''high temperature (HT) and low temperature (LT) interface'' here because of the incompleteness of the transition of the compound under study.

In our previous works we pointed out the irreversible character of the propagation of the interface in isothermal conditions, which is inherent to the metastable character of the initial state. In the present work we address the problem of the control of the interface motion by an external command parameter. Our study was performed on single crystals of the SC compound [{Fe(NCSe)(py)$_2$}$_2$(m-bpypz)], where py designates pyridine and bpypz designates 3,5-bis(2-pyridyl)-pyrazolate, [12] which was revealed to be rather robust under repeated thermal cycling.

The preparation of the crystals was described by K. Nakano *et al.* [12,13]. We actually investigated a large number of crystals of various shapes. The best data, shown here, were obtained with elongated platelets, typically a few 100 μm long. We first selected ∼20 of them for performing magnetic measurements in a physical property measurement system device; see Fig. 1. The data evidence a square-shaped hysteresis loop associated with the first-order spin transition, ∼5 K wide.

We show in Fig. 2 typical images obtained during the on-cooling and subsequent on-heating transitions of a fresh crystal. The nucleation of the LT phase (on cooling) started in the right part of the crystal, that of the HT phase (on heating) at the right tip, and the orientation of the
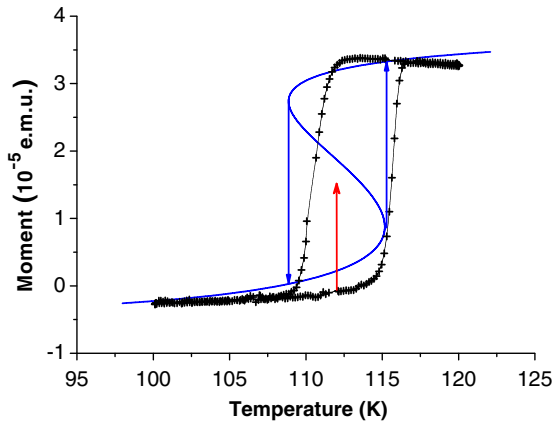
FIG. 1 (color online).   Magnetic moment measured with a set of [{Fe(NCSe)(py)$_2$}$_2$(m − bpypz)] tiny crystals, under external field 5000 Oe. Temperature sweep rate was ± 1 K/min. The data were not corrected for diamagnetism. The blue line reports the hysteresis loop associated with the static limit of the dynamical model used for Fig. 5. The red arrow stands for the light-induced creation of the HT and LT interface reported in the following.

macroscopic frontline remained constant for both processes. Such a simple behavior was typical of high-quality fresh crystals, and it could be repeated several times before major alterations (cracks) of the crystal. In a given crystal, most often the HT → LT and LT → HT frontlines propagated in opposite ways. In the case of a large assembly of randomly oriented crystals, we observed frontlines propagating in various senses, which ruled out the existence of a sizable temperature gradient in the sample cell, as a possible driving force of the ST. For all good-quality crystals we observed a preferred orientation of the frontline with respect to the edges of the crystal, at an angle ~125°. The spatial variation of the emerging intensity, in the (x, y) plane (see Fig. S2 in the Supplemental Material) [14], can

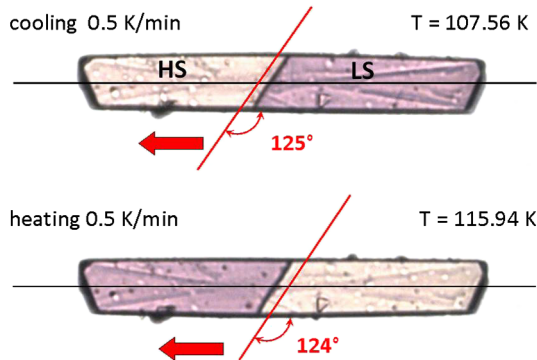be reasonably interpreted in terms of an interface profile and make it possible to determine the width of this (macroscopic) interface, ~7 μm (full width). The oscillations of the emerging intensity on both sides of the interface are assigned to optical effects resulting from the impact of the mechanical stresses upon the refractive index of the material [9].

We reported in Fig. 3 the propagation data (interface position vs time) [9], recorded during the on-cooling and on-heating transitions, located in the [107.66–107.44 K] and [115.90–115.98 K] temperature ranges, respectively. These propagation data determine fairly constant velocities, ~6.1 and 26.2 μm s^{-1}, for the on-cooling and on-heating transformations, respectively. The videos are reported in the Supplemental Material [14]. The different velocities observed for the cooling and heating processes are to be discussed in terms of the elastic properties of the HT and LT phases. It seems easier to grow nuclei of a soft phase inside a stiffer one than the reverse. The present suggestion is supported by recent simulations using a deformable Ising model [15]. An extensive study, not reported here, showed that the data are crystal dependent, with usually smaller velocity values, in the range 1–10 μm s^{-1}, but with a heating:cooling velocity ratio close to 10:1. The relatively large values of the interface velocity in the present crystal presumably originate from a high-structural quality, associated with a large hysteresis interval, which is supported by its exceptionally robust character.

Thanks to the lack of structural damage, we could undertake experiments aiming to test the reversibility of the interface motion. Our first attempts were based on a rapid raise of the set value of the temperature controller, as soon as the growth of the LT phase was detected, but very soon we discovered that the extension of the LT area was
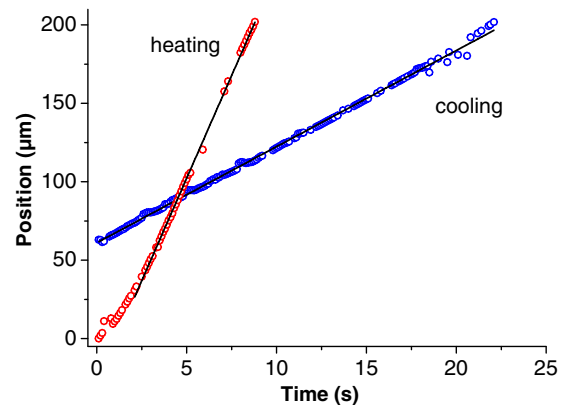

FIG. 2 (color online).   Transmission images of a high-quality crystal of {Fe(NCSe)(py)$_2$}$_2$(m-bpypz), in the course of its first on-cooling and on-heating thermal spin transitions, showing the macroscopic HT and LT interfaces. Crystal length was ~200 μm. The corresponding movies are in the Supplemental Material [14].

FIG. 3 (color online).   Propagation plots for HT ↔ LT interface during the first on-cooling and on-heating transitions of the [{Fe(NCSe)(py)$_2$}$_2$(m-bpypz)] selected crystal, leading to the propagation velocity values (along the long axis of the crystals): 6.1 and 26.2 μm/s for the on-cooling and on-heating transitions, respectively.

P H Y S I C A L   R E V I E W   L E T T E R S

efficiently prevented by a simple increase in the intensity of the irradiation beam of the microscope. We could easily stop the interface motion by fine-tuning the power delivered by the source of light, and then we drove the system inside the spontaneous hysteresis interval (that is, approximately, the hysteresis interval obtained with a weak illumination intensity). The photocontrol of the interface motion revealed to be almost free from sizable inertia effects that are the major drawback of the alternative control by temperature.

The photocontrol of the interface is a new effect that was not expected from simple simulations based on the macroscopic mean-field equation including a photoexcitation term, as it was introduced in the 1990s for modeling the light-induced thermal instability [16]. A detailed calculation of the photoeffect (including both low-high and high-low relaxation terms [17]) is given in the Supplemental Material [14] and shows that the down shift of the transition temperature under the effect of light should be negligible. Therefore we suggest an alternative explanation in terms of a mere photothermal effect. The actual temperature of the crystal is higher than its apparent temperature, that is, the "bath temperature" given by the temperature controller. In the reported experiment, above a sufficient intensity of light, the actual temperature of the crystal reached the transition temperature in the heating mode (T_{up}) and nucleation of the HT phase started. The growth of the HT phase was stopped by a rapid return to the minimum intensity value, which obviously induced a cooling of the crystal down to its initial temperature. For supporting the present idea of a photothermal effect, we undertook a systematic investigation of the apparent transition temperatures of a group of crystals, illuminated at various intensities, in exchange gas or in vacuum. As expected we found that the transition temperature interval was sizably down shifted under the effect of large intensities. The maximum amplitude of the effect was of a few K in the presence of exchange gas, but it was strongly increased in vacuum. Then, approximately half of the crystals were trapped in the HT state at the apparent temperature of 65 K, and they rapidly switched to the stable LT state when light was switched off. The amplitude of the photothermal effect in the different crystals was visibly scattered in the in-vacuum experiment and was crucially dependent of the crystal thickness. Generally speaking, the photothermal effect is suitable for an accurate control of the interface motion, and should be efficient in all kinds of switchable crystals.

We now focus on a first application of the control of the HT and LT interface, which consists of investigating the interface velocity inside the thermal hysteresis loop. We illuminated the crystal in the LT state, at 112 K, near the equilibrium temperature, as schematized in Fig. 1. With a sufficient intensity, after a brief while, a macroscopic domain was generated at the right tip of the crystal, and

the front line moved rapidly as long as the strong illumination was on. This way we drove the interface to the center of the crystal and we immediately reduced the illumination power to its minimum value. Then the interface was left at equilibrium, basically. In other words the crystal was left in a stable biphasic state. To the best of our knowledge, the first time in the field of switchable molecular solids. The video of this experimental sequence is in the Supplemental Material [14]. The effect of the minimum intensity—which is needed for recording images—will be neglected in the following, and the corresponding hysteresis interval will be termed "spontaneous" hysteresis. We performed measurements of the interface velocity under the minimum intensity at different temperatures inside this spontaneous hysteresis interval. After each isothermal stage, we drove the interface to its initial position by suitable variations of intensity and temperature, in order to explore the same part of the crystal at all temperatures.

The data shown in Fig. 4 are quite suggestive. They were obtained in two runs: we first followed the interface position at 112, 112.7, 111, and 110 K. The velocity rapidly increased on approaching the tip of the crystal, and for this reason we lost the interface, that is, the crystal totally turned to LT. We assigned the final velocity increase to the presence of defects. In a second run we determined the interface velocity at 113 and 114 K, and visibly the data of the second run are not perfectly in line with those of the first run. The "clean" zone of the crystal suitable for the velocity determination was getting smaller and smaller, and subsequent runs did not provide any more reliable data. This set of experiments showed that the macroscopic interface remains out of equilibrium inside the whole hysteresis temperature interval, except for a central temperature that is easily identified to the static equilibrium
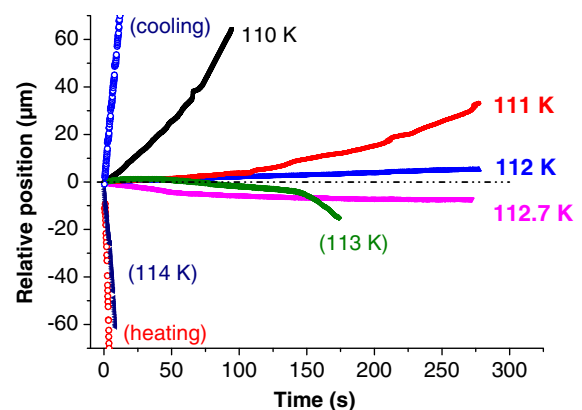

FIG. 4 (color online). The propagation of the HT and LT interface in a high-quality crystal of [{Fe(NCSe)(py)$_2$}$_2$(m-bpypz)], monitored at constant temperatures inside the thermal hysteresis interval (the position data have been slightly shifted in order to have a common origin, for clarity). The temperature values inside brackets correspond to the second experimental run. The data of Fig. 3 are reported for comparison (open symbols).

temperature, that is, the Maxwell point of the first-order transition, which is associated with the null velocity of the interface. The experimental value ~ 112.6 K is slightly higher than the average of the switching temperatures shown in Fig. 2, which is ~ 111.7 K. We point out that this is the first direct access to the equilibrium temperature of a hysteretic system in the spin-crossover literature. A similar use of out-of-equilibrium properties for determining the unstable equilibrium branch was recently reported in a low-temperature investigation of $\{[\text{Fe}(\text{bbtr})_3](\text{BF}_4)_2\}_\infty$ single crystals by optical spectroscopy [18], but without the present access to spatiotemporal properties.

The temperature dependence of the interface velocity can be understood by a simple inspection of the dynamic mean-field potential $U(n_{\text{HT}}, T)$, which originates from the resolution of a stochastic master equation of an Ising-like model [19]. We have calculated $U(n_{\text{HT}})$ at different temperatures inside the thermal hysteresis loop; see Fig. 5. The basic idea is that the interface velocity is governed by the jump frequencies over the macroscopic energy barriers of the dynamic potential. Calculations were performed analytically [19], using the complete macroscopic mean-field master equation that accounts for both $\text{HT} \rightarrow \text{LT}$ and $\text{LT} \rightarrow \text{HT}$ processes in a thermal activation regime [17] as follows (with the HT fraction n_{HT} abbreviated by n for simplicity):

$$dn/dt = -nk_{\text{HL}} + (1-n)k_{\text{LH}} = -\partial U / \partial n \quad (1)$$

with $k_{\text{HL}}(T, n) = k_\infty \exp(-\beta E_{\text{HL}} - \alpha n)$; $k_{\text{LH}}(T, n) = gk_\infty \exp(-\beta E_{\text{LH}} + \alpha n)$, where $\beta = 1/T$, $\alpha = 2J/T$ is the self-acceleration parameter [20], J is the interaction constant in Ising-type model [19,21], $g = g_{\text{HT}}/g_{\text{LT}}$ is the degeneracy ratio, k_∞ is the scaling factor of the relaxation rate constants, and E_{HL} and E_{LH} are the molecular barrier energies with $E_{\text{HL}} - E_{\text{LH}} = \Delta$ the molecular energy gap.
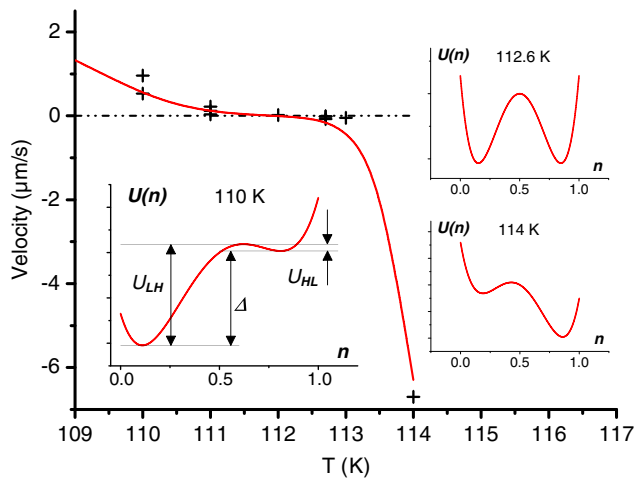

FIG. 5 (color online). The calculated velocity (at adapted scale) compared to the experimental data of Fig. 4 Insets: the mean-field dynamic potential $U(n)$ computed at several temperatures around the equilibrium temperature 112.6 K.

For simplicity, all energies are expressed in temperature units. By simple integration of Eq. (1) at constant temperature T, the analytical expression of the dynamic potential is obtained as follows:

$$U(T, n) = -[n/2\beta J + 1/4\beta^2 J^2]k_{\text{HL}} - [1/2\beta J - n/2\beta J + 1/4\beta^2 J^2]k_{\text{LH}}. \quad (2)$$

The parameters values for the calculations were determined as follows: $\ln g = 5$, leading to entropy change upon complete transformation $\Delta S = R \ln g \sim 40$ J K^{-1} mol^{-1}, a value reduced with respect to typical literature values (50–70 J K^{-1} mol^{-1}) due to the specific character of the transition where only 2/3 molecules undergo the spin crossover. The electronic gap was derived from the equilibrium temperature, $\Delta = T_{\text{eq}} \ln g \sim 563$ K. The value of the interaction parameter, $J = 138$ K, was tuned so as to obtain a quasistatic hysteresis loop ~ 6 K wide (reported in Fig. 1), and that of the energy barrier value, $E_{\text{HL}} = 1150$ K, so as to result in the measured value of the thermal return temperature, T(LIESST) [22], ~ 60 K (unpublished result).

The height of the dynamic barrier is straightforwardly derived from the double-well shaped curves shown in Fig. 5, where the stable, metastable, and unstable states are easily recognized at each temperature. The values of the macroscopic barriers U_{HL}, U_{LH} obviously follow, as well as the lifetimes, τ_{HL} and τ_{LH}, of the associated metastable states, which are proportional to $\exp(\beta U_{\text{HL}})$ and $\exp(\beta U_{\text{LH}})$, respectively. The front velocity is the net result of two opposite processes, which are assumed to be proportional to the inverse lifetimes of the HL and LT states:

$$v = A[(1/r)\exp(-\beta C U_{\text{HL}}) - r\exp(-\beta C U_{\text{LH}})] \quad (3)$$

where the energy constant C and velocity constant A have been inserted for homogeneity reasons. The preexponential factors r, $1/r$, may be understood in terms of effective degeneracies associated with the different elastic properties of the HT and LT phases. With the set of parameter values $C = 150$ K, $r = 8$, we obtained a good overlap to the experimental data, which is shown in Fig. 5. The shape of the velocity vs temperature plot was very sensitive to the parameter values. The amplitude of the plateau and the asymmetry of the curve are separately governed by parameters C, r, respectively. This resulted in a rather accurate determination ($\pm 10\%$) of the macroscopic barrier associated with the thermal hysteresis, $CU_{\text{HL}}(T_{\text{eq}}) = CU_{\text{LH}}(T_{\text{eq}}) \sim 800$ K per molecule, that is, ~ 7.5 kJ mol^{-1}.

We have investigated the motion of the macroscopic interface that is generated by the thermal transition of a robust spin-crossover crystal and showed that the motion of the interface could be photocontrolled by the source of light of the microscope, through a suggested photothermal mechanism. We used the photocontrol method for generating biphasic states, so as to determine the interface velocity as a function of temperature inside the thermal hysteresis

loop. We successfully modeled the data by a simple dynamical mean-field model. The present experiment gave direct access to the equilibrium temperature (Maxwell point), and the height of the macroscopic energy barrier was determined in the frame of the model. On one hand, the use of light as a flexible command parameter should open the way to research physics of spin domain walls and of their interactions with defects. On the other hand, stabilization of biphasic (that is, multidomain) states paves the way to near-field investigations of like-spin domains, which are very slow techniques. These new research fields might be as exciting and fruitful as the field of ferromagnetic domains has been during the past century.

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