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Spin Crossover

Structure-Driven Orientation of the High-Spin–Low-Spin Interface in a Spin-Crossover Single Crystal**

Mouhamadou Sy, François Varret,* Kamel Boukheddaden,* Guillaume Bouchez, Jérôme Marrot, Santoshi Kawata, and Sumio Kaizaki

Abstract: *The orientation of the high-spin (HS)–low-spin (LS) macroscopic interface at the thermal transition of thin [{Fe(NCSe)(py)$_2$}$_2$(m-bpypz)] crystals is explained by considering the possible vanishing of the structural mismatch between the coexisting phases. The structural property which allows mismatch-free interfaces is characterized. The observed orientations of the interface and the tilt angle between the HS and LS domains are accurately reproduced by a two-dimensional continuous medium model, based on the structural data. Simulations using an atomistic electro-elastic model meet the predictions of the macroscopic analysis and provide information on the distribution of the elastic energy density in the biphasic state. The presence of mismatch-free domain structures can explain the exceptional resilience of these crystals upon repeated switching.*

Switchable molecular solids are known to display first-order phase transitions under the effect of cooperative elastic interactions between their labile molecular units. The thermal transition of spin-crossover solids[1] was recently investigated by optical microscopy,[2] which evidenced the propagation of a macroscopic interface between high-spin (HS) and low-spin (LS) phases. We observed that the stresses generated by the structural change at the transition may be quite large and induce major structural defects.[2b] As a matter of fact, the resilience of spin-transition crystals upon repeated switching crystals is extremely variable.[2d] For a given compound it depends on the crystal quality (low-quality crystals are more brittle) and on the crystal size (large crystals develop larger stresses) and presumably on the type of the chemical bonding (π–π stacking, covalent bonding, etc.). We recently investigated thin crystals of [{Fe(NCSe)(py)$_2$}$_2$(m-bpypz)], where py = pyridine and bpypz = 3,5-bis(2-pyridyl)-pyrazolate,[3] here abbreviated Fe(NCSe), some of which revealed to be exceptionally resilient to repeated switching (> 100 times). At variance from all our previous observations,[2b–d] Fe(NCSe) crystals exhibited straight and narrow HS LS interfaces along well-defined and reproducible orientations.[4] Generally speaking, it is clear that the amplitude of elastic stresses at the transition crucially depends on the interface orientation, and that the observed orientations minimize the elastic energy of the system. We therefore postulated that the exceptional resilience of thin Fe(NCSe) crystals might be due to the vanishing of elastic stresses between the spin phases. Here we show that “mismatch-free” interface orientations can be derived from the structural data of Fe(NCSe). We used a two-dimensional continuous medium analysis, suited to thin crystals, which accurately meets the experimental data. We also used a discrete approach for obtaining detailed information on the spatial distribution of the elastic energy.

We investigated by optical microscopy a thin and narrow crystal of Fe(NCSe), see Figure 1. Most often we observed a single LS HS interface as shown in Figure 1 a. We also show complex domain structures generated by intense photothermal effect, see Figure 1 b,c. We indeed currently investigate the effects of the temperature changes induced by light and so far we predicted that it can lead to stabilize the HS LS interfaces.[5] This is illustrated here by the onset of multiple interfaces, and the complex domain structure characterizes the possible two orientations of the interface. The thermody-

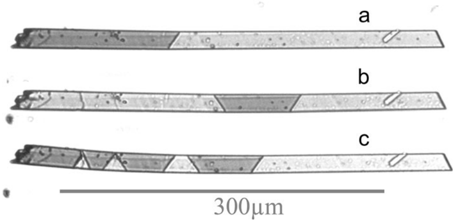

Figure 1. Top view images of a thin and narrow single crystal of Fe(NCSe), about 385 μm long, during the on-cooling transition at 105 K (a) and on cooling down to 65 K under intense shining (b,c).

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[*] M. Sy, Prof. em. F. Varret, Prof. K. Boukheddaden, G. Bouchez
Groupe d’Etude de la Matière Condensée, Université de Versailles
CNRS UMR 8635, 45 Avenue des Etats-Unis
78035 Versailles Cedex (France)
E-mail: fvarret@physique.uvsq.fr
kbo@physique.uvsq.fr
Ing. J. Marrot
Institut Lavoisier, Université de Versailles
CNRS UMR 8180 45 Avenue des Etats-Unis
78035 Versailles Cedex (France)
Prof. S. Kawata
Department of Chemistry, Faculty of Science
Fukuoka University
Nanakuma, Jonan-ku, Fukuoka 814-0180 (Japan)
Prof. em. S. Kaizaki
Department of Chemistry, Graduate School of Science
Osaka University, Toyonaka, Osaka, 560-0043 (Japan)

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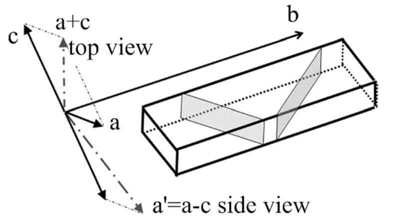
namic description of an interface under photo-thermal effect is briefly discussed in the Supporting Information. The photo-thermal effect was obtained here under the maximum intensity of the microscope source providing to the crystal a specific power of about 50 mW cm^{-2} (see the Supporting Information). The apparent transition temperature of the crystal was severely smeared out and lowered by about 30–40 K. It is useful to remark here that measuring the real temperature of the crystal under illumination is an interesting issue. Indeed, the measured temperature in the experiment is that of the bath (apparent temperature), however the presence of a "static" interface is an indication that the system is locally at the transition temperature, although the latter is sensitive to photo-excitation effects. In the present situation, however, the photo-excitation effects are expected to be negligible because of the large difference between the transition temperature (T_{eq} about 112.5 K) and the LIESST (Light-excited Spin-State Trapping Temperature) relaxation temperature, T_{LIESST} about 50–60 K for this compound. A direct estimate of the magnitude of the photo-heating is made in the Supporting Information. The key feature of the transmission images of Figure 1 is the straight and narrow character of the borderlines which implies planar interfaces, oriented perpendicular to the large faces of the crystal, see Scheme 1. The angle between the interface projection and the long axis of the platelet is $\approx$56–57°, a value close to the 60° value previously reported for thicker crystals of this compound.[4] The tilt angle of the long axis of the crystal was accurately determined (1 ± 0.1°). We also obtained a side view of a similar crystal (see Figure S1 in the Supporting Information) which confirmed the said orientation of the interface. All images were obtained using a microscope Nikon Eclipse LV100 (objective × 5, numerical aperture NA = 0.15) connected to a digital camera Coreview Dalsa Falcon 1.4 M100 HG color.



Scheme 1. The crystallographic axes of Fe(NCSe) with respect to the crystal habits.[6] The observed orientations of the interface are shown as shaded areas. The dotted arrows represent the possible two orientations of the microscope axis.

Table 1: Crystallographic data associated with the thermal transition of Fe(NCSe): average values in the hysteresis range (about 90–100 K), see the Supporting Information for details. The standard deviations in the HS phase are negligible with respect to the LS phase. The key feature here is the opposite variations of b and a', due to the large change in β.

	a [Å]	*b* [Å]	*c* [Å]	β [°]	*a'* [Å]
HS phase	13.207	9.367	14.910	96.677	21.037
LS phase	13.123 (40)	9.132 (16)	14.853 (34)	99.006 (18)	21.304 (53)
difference	0.08 3 (44)	0.236 (18)	0.057 (36)	−2.329 (19)	−0.268 (57)

We develop here a simple structural analysis in the frame of continuous media, aiming at characterizing a structural plane globally invariant at the transition, that is, leading to a mismatch-free HS–LS interface. It is worth noticing that exact interface matching is only casual for 3D systems: the number of equations to be fulfilled is three (invariance of a planar unit cell defined by two parameters and one angle) while the number of degree of freedom is only two (the polar angles of the normal to the interface plane). But, an ideally thin sample is represented by a 2D system which allows the desired interface matching, since the number of equations to be fulfilled (one for invariance of interface length) equals the number of degrees of freedom (one for interface orientation). The analytical approach of the problem is described below. It may be useful to notice 1) the conservation of interface length leads to a second-order equation providing 2, 1 or 0 solutions; 2) for a rectangular lattice, opposite expansions of the unit cell parameters obviously lead to mismatch-free orientations.

The mismatch-free orientations are researched by considering the relative expansion of a real space vector $\mathbf{L}=\mathbf{a}\sin\theta\cos\phi+\mathbf{b}\sin\theta\sin\phi+\mathbf{c}\cos\theta$. The vectors **a, b, c** are the basis vectors of the structure, which vary at the transition. On the contrary, the reduced coordinates $\sin\theta\,\cos\phi$, $\sin\theta\,\sin\phi$, $\cos\theta$, define a structural orientation, that is, a vector linked to the atomic positions. They consequently are conserved at the transition. The modulus, L, of $\mathbf{L}$ is straightforwardly calculated (using the matrix associated with the scalar product operator) and allows deriving the relative expansion $\delta L/L$ upon the LS→HS transformation. The mismatch-free orientations are found when $\delta L/L$ vanishes. We used the structural data listed in Table 1, derived from the set of crystallographic data[8] at 90, 98, 101, 155, 200 K, see the Supporting Information. We explored the basal plane (101) of the platelets, by using $\mathbf{L}=\mathbf{a}'\cos\theta'+\mathbf{b}\sin\theta'$. The resulting curve $\delta L/L=f(\theta')$ is shown in Figure 2. It obeys the mirror property with respect to **b** in the crystal plane. The resulting predictions, see Table 2, are in excellent agreement with the experimental data, including the tilt angle which is obtained with the correct sign and magnitude.

Along the direction $\mathbf{a}+\mathbf{c}$ perpendicular to the basal plane $\delta L/L$ is large (about 0.023). The presence of finite thickness will tend to shorten the interface, so as to reduce its elastic energy, that is, to slightly turn the interface towards the short axis ($\mathbf{a}'$). This may explain the slightly larger values of the ($\mathbf{L}$, $\mathbf{b}$) angle reported for thicker crystals.[4] It is worth noting that

Table 2: The mismatch-free orientations derived from Figure 2, and the resulting tilt angle ε (calculated with angle values < 90°). For standard deviations, see the Supporting Information. The angles are expressed in degrees.

	θ'	$\psi_{\mathrm{LS}}=(\mathbf{b},\mathbf{L})_{\mathrm{LS}}$	$\psi_{\mathrm{HS}}=(\mathbf{b},\mathbf{L})_{\mathrm{HS}}$	$\varepsilon=\psi_{\mathrm{HS}}-\psi_{\mathrm{LS}}$
predicted	58.22 (3.7)	55.3 (3.9)	54.3 (3.9)	−1.0 (±0.1)
experimental		≈57° (±1)	≈56 (±1)	−1.0 (±0.1°)

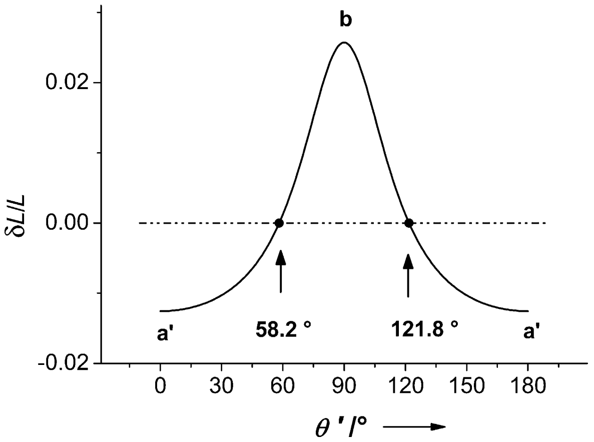


Figure 2. Relative expansion in the basal plane (**a′**,**b**). Arrows indicate the mismatch-free orientations.

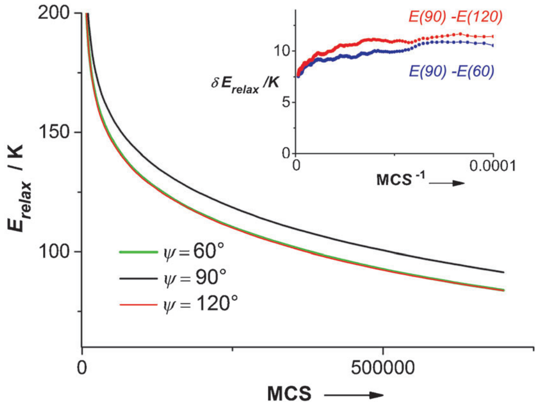


Figure 3. The kinetics of relaxation of the elastic energy, for different interface orientations (ψ values). In the inset, the enlarged energy differences $[E_{\text{elas}}(\psi{=}90°)-E_{\text{elas}}(\psi{=}60°)]$ and $[E_{\text{elas}}(\psi{=}90°)-E_{\text{elas}}(\psi{=}120°)]$, for extrapolation to an infinite number of MCS, is shown.

the presence of structural defects, or temperature gradients in case of rapid temperature change, may disturb the onset of stress-free interfaces and consequently tend to reduce the resilience of the crystals.

We now develop a microscopic approach of the problem, based on an anisotropic extension of our recent electro-elastic model,[8]using a simple one-site model suited to the atomic structure of the crystal (see the Supporting Information). We introduce anisotropic local properties through the equilibrium distances of the nearest (nn) and next-nearest (nnn) neighbor pairs. For so doing, we consider a discrete rectangular lattice based on a (**b**, **a′**) elementary cell, defined by the crystallographic data of Table 1. The HH (HS–HS) and LL (LS–LS) equilibrium distances are straightforwardly determined in the HS and LS phases, respectively. Those for mixed pairs HL (HS–LS) = LH (LS–HS) are taken by averaging the HH and LL equilibrium distances in the same orientation, see Table 3. A detailed description, including the Hamiltonian of the model, is given in the Supporting Information.

Table 3: Equilibrium distances of HH, LL, and HL pairs in different orientations.

Nature	Orientation	R_0^{HH} [Å]	R_0^{LL} [Å]	R_0^{HL} [Å]
nn	Ox(b)	9.37	9.13	9.25
nn	Oy(a′)	21.04	21.30	21.17
nnn	oblique	23.03	23.17	23.10

Monte Carlo simulations were performed on a 20×120 rectangular lattice with free boundary conditions. The system was set at null temperature, in a frozen biphasic spin state. Initial distances were those of a homogeneous state (HS). The HS and LS states were defined on either side of a straight borderline passing through the center of the system with various orientations, see the Supporting Information (Figure S3). The orientation angle is defined here $\psi = \psi_{\text{HS}} = (\mathbf{b}, \mathbf{L})_{\text{HS}}$ in the initial state. Initially we aimed at observing the spontaneous rotation of the interface towards its equilibrium orientations. However, the kinetics of the model, in terms of Monte Carlo spin–lattice steps revealed to be extremely slow, and we turned to scan the "relaxed" elastic energy of the spin-frozen system as a function of the interface orientation.

In Figure 3 we show the evolution of the total elastic energy as a function of the number of lattice Monte Carlo steps (MCS), for selected ψ values. Differences in the elastic energies appeared when most of the initial excess energy was released. The kinetic curves are in shape of stretched exponentials and do not allow an accurate determination of their asymptotic values. Therefore we plotted in Figure 3 (inset) the evolution of energy differences, which obviously have reached their asymptotic values. Based on this observation we have plotted the relaxed elastic energy as a function of ψ, see Figure 4. This plot is representative of the angular dependence of the completely relaxed elastic energy, save for a constant shift. Stable positions are obtained for $\psi = 60°$, 120°, which fairly agree with the experimental data, as well as with the predictions of the continuous medium model. We would like to mention here that the symmetric character of this macroscopic elastic energy profile does not mean any symmetry between the HS and LS atomic states, which on the contrary differ due to the ligand field contribution.

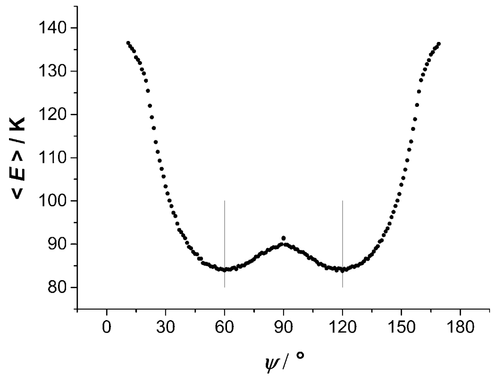


Figure 4. The relaxed elastic energy as a function of the interface orientation, after 700 000 MCSs.

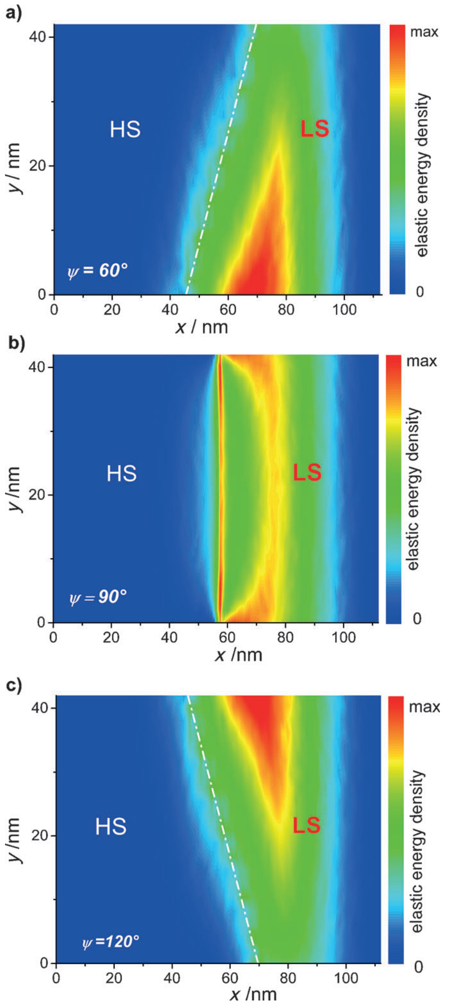


Figure 5. Maps of the relaxed elastic energy after 700 000 MCS for different interface orientations (at the same energy scale). The white line visualizes the position of the HS–LS interface.

We also determined the tilt angle and found 0.8°, a value close to the prediction of the continuous medium model, see the Supporting Information for details. In Figure 5 we mapped the density of elastic energy in the relaxed state, for the orientation values $\psi = 60°$, 90°, 120° associated with the extrema of the energy plot of Figure 4. For $\psi = 90°$ (Figure 5 b) the energy density peaks at the close vicinity of the interface; the diffuse maximum in the right part of the figure, which is slowly decreasing on increasing the number of MCS, has to be assigned to the incomplete character of relaxation. For $\psi = 60°$, 120° (Figure 5 a,c, respectively), broad maxima are also observed and assigned as well to the incomplete relaxation, but the density no longer peaks at the interface. It is inferred that 1) the elastic energy at equilibrium is mainly located at the interface, in agreement with previous theoretical work,[8] and 2) this interface energy almost cancels out for the orientations predicted by the continuous medium model.

To summarize, the presence of well-defined orientations of the HS-LS interface observed in Fe(NCSe) thin crystals has been correlated to the structural data. They are associated with mismatch-free interfaces, which appear to be the key factor of the exceptional resilience of the crystals upon repeated switching.

CCDC 983837, 983838, 983839 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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