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Nanoindentation Reveals Drastic Elastic Softening in a Spin Crossover Molecular Crystal

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Abstract. Spin-crossover molecular crystals exhibit a unique interplay between electronic and structural degrees of freedom, yet their mechanical response remains poorly understood. In this study, we employ variable-temperature nanoindentation to quantify elastic modulus and hardness of single crystals of the molecular complex $[\text{Fe}_{0.89}\text{Zn}_{0.11}(\text{bpp})_2](\text{BF}_4)_2$ (bpp = 2,6-bis{pyrazol-1-yl}pyridine) across the thermally induced first-order spin transition. Our results reveal a sharp and reproducible elastic anomaly: within a narrow interval near the transition temperature (249 ± 1 K), the reduced modulus drops to a pronounced minimum (~ 2.0 GPa), contrasting sharply with the values observed in the high spin (4.5 ± 0.3 GPa) and low spin (7.0 ± 0.5 GPa) states. This elastic softening is mirrored in the hardness, which otherwise remains comparable in the two spin states. At the transition point, the load-displacement curves display large hysteresis loops, revealing strong time-dependent deformation and enhanced energy dissipation. Crucially, the indentation does not induce a persistent spin-state change, suggesting the observed anelastic softening arises from molecular-scale spin-state relaxation rather than nucleation and growth mechanisms. On the other hand, the marked difference in modulus between the two spin states is not a relaxation effect, it is attributed to the substantial variation in crystal density accompanying the transition. These findings establish nanoindentation as a powerful method for probing the mechanical properties of spin crossover materials, offering valuable insights for their applications in mechanical sensors, actuators, mechanocaloric and energy harvesting devices.

Introduction

Molecular spin-crossover complexes of transition-metal ions such as Fe^{2+} , Fe^{3+} , Co^{2+} , Co^{3+} , Mn^{2+} , Mn^{3+} , and Cr^{2+} are well known for their ability to reversibly switch between the low-spin (LS) and high-spin (HS) electronic configurations of the metal center. The spin transition can be triggered by various external stimuli, including temperature, mechanical stress, light irradiation, or small molecule adsorption, and is accompanied by pronounced changes in optical, magnetic, electrical, and structural properties [1–4]. One of the most remarkable features of SCO materials in the solid state is the significant change in mass density associated with the spin transition. Upon transformation from the HS to the LS state, the shortening of metal-ligand bond lengths typically induces volume contractions of a few percent, although values as high as 15–22% have been reported in extreme cases [5]. Over the past decade, this pronounced and reversible lattice strain has stimulated growing interest in the development of SCO-based mechanical transducers for applications in actuation, sensing, thermal management and thermal energy harvesting [6–11].

The realization of such mechanically responsive systems has clearly demonstrated the capacity of SCO materials to convert molecular-scale spin switching into measurable mechanical motion in both micro- and macroscopic devices. However, mechanical property characterization has revealed that their behavior cannot be described solely in terms of simple elastic deformation. Instead, a pronounced anelastic response is often observed, involving time-dependent strain, elastic softening, and enhanced energy dissipation [12]. Although similar effects are common in materials undergoing structural phase transitions [13], they were not initially anticipated or quantitatively explored by the SCO community.

Indeed, despite the central role of lattice strain in the SCO phenomenon, quantitative data on the elastic properties of SCO materials remain still scarce. In most reported studies, mechanical parameters were determined in only one of the two spin states. This limitation largely arises from the fact that bulk SCO materials are commonly obtained as powders or small single crystals, which are not well suited to conventional mechanical testing techniques. Consequently, most available elastic data have been derived from high-pressure X-ray diffraction experiments [14–15], yielding bulk moduli. Other approaches, such as resonant ultrasonic spectroscopy [16–18], nuclear inelastic scattering [19], Brillouin scattering [20], atomic force microscopy [21–22], and micromechanical resonators [23–24], have also been employed, although in several cases measurements were performed on thin films rather than bulk crystals. Reported elastic moduli (Young's modulus or bulk modulus) of crystalline SCO compounds generally lie in the range of 1–20 GPa, with typical values between 5 and 10 GPa. As expected from its higher density, the LS phase is consistently stiffer than the HS phase. In addition, information related to elastic properties (e.g., Debye temperature) has been extracted from laboratory Mössbauer spectroscopy measurements [25]. Mechanical testing of freestanding SCO@polymer composite films has also been reported [12], but such measurements do not provide access to the intrinsic elastic constants of the SCO phase.

In the present work, we explore the use of nanoindentation to investigate the mechanical properties of single crystals of a molecular SCO complex. In this technique, a sharp indenter is pressed into the surface of a specimen while continuously recording the applied load and the corresponding penetration depth. Analysis of the resulting load–displacement curve provides quantitative access to hardness and elastic modulus [26–33]. A typical nanoindentation cycle is illustrated in Figure 1a. During loading, the applied force P is progressively increased while the

indentation depth h is recorded. Once the maximum load P_{max} is reached, unloading is performed and the indenter displacement is monitored continuously. In standard analysis, loading is assumed to include both elastic and plastic contributions, whereas unloading is considered to reflect purely elastic recovery [26].

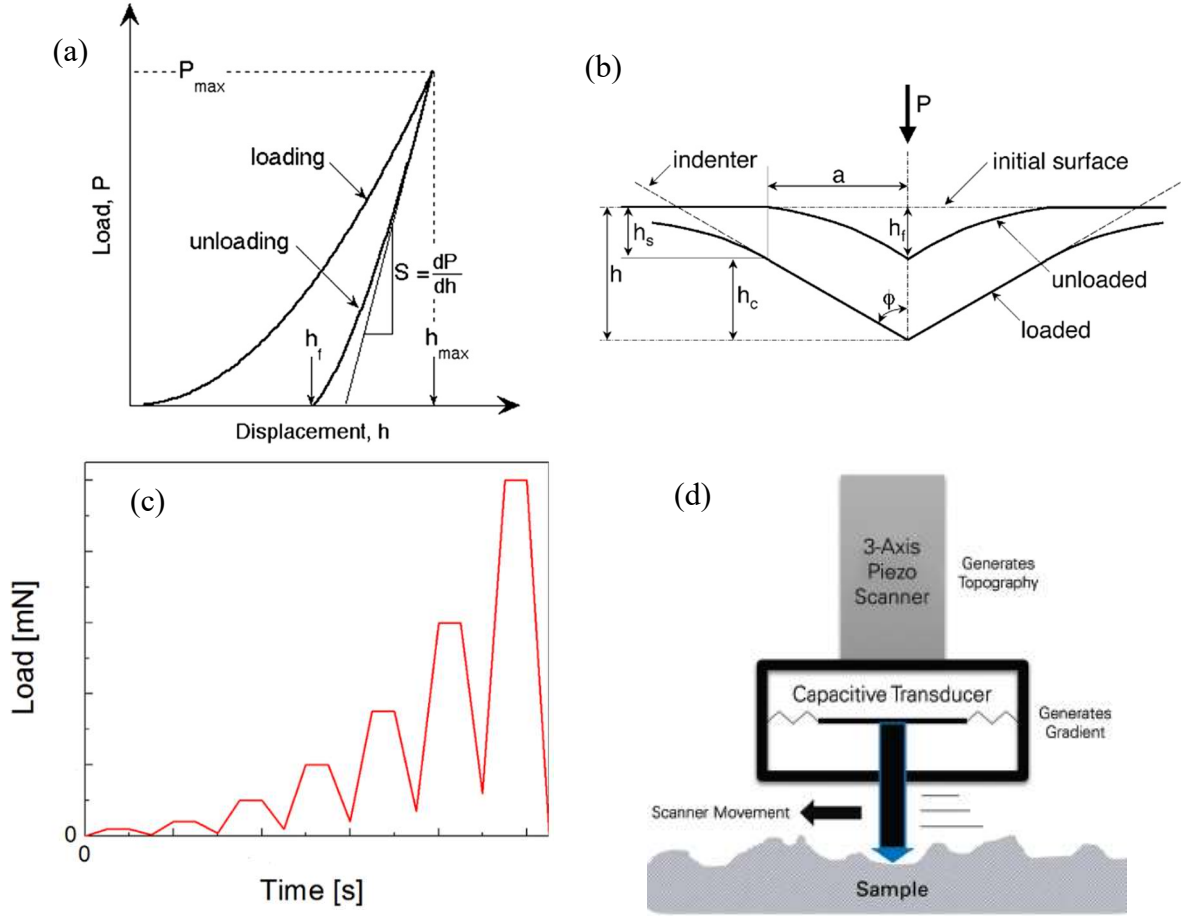


Fig. 1. (a) Typical load-displacement curve and (b) cross-section of an indentation. (c) Typical load function used in partial unloading experiments. (d) Scheme of in-situ surface topography imaging using the indenter tip.

The maximum indentation depth (h_{max}) together with the initial unloading contact stiffness ($S = dP/dh$) form the basis for calculating both hardness and elastic modulus using the method introduced by Oliver and Pharr [26]. A key quantity in their analysis is the contact depth (h_c), which defines the depth of material in direct contact with the indenter (see Figure 1b) and the associated projected contact area (A). For a Berkovich indenter, the projected area is expressed as:

$$A(h_c) \approx 24.5h_c^2 \quad (1)$$

with

$$h_c = h_{max} - 0.75 \frac{P_{max}}{S} \quad (2)$$

Once the contact area is known, hardness is calculated as the mean contact pressure under the maximum applied load:

$$H = \frac{P_{max}}{A} \quad (3)$$

whereas the reduced modulus of the material is obtained from the initial unloading stiffness according to:

$$E_r = \frac{\sqrt{\pi}}{2\sqrt{A}} S \quad (4)$$

The reduced modulus is related to the specimen's elastic modulus by:

$$\frac{1}{E_r} = \frac{(1 - \nu_i^2)}{E_i} + \frac{(1 - \nu^2)}{E} \quad (5)$$

where E and ν are the Young's modulus and Poisson's ratio of the specimen, and E_i and ν_i are those of the indenter. For a diamond indenter, $E_i = 1140$ GPa and $\nu_i = 0.07$. Since $E_i \gg E$, the first term on the right-hand side can be neglected and (for usual values of the Poisson's ratio between 0.2 and 0.4) one can make the rough estimation that $E \approx 0.90(\pm 0.05)E_r$.

Because nanoindentation probes a confined subsurface volume in a locally destructive manner, several experimental constraints must be considered. First, the crystal thickness must be sufficient, typically several micrometers, to minimize substrate effects. Second, the surface must be flat, smooth, and laterally extended to allow multiple independent indentations. In practice, crystals with lateral dimensions below approximately 200 - 300 μm were found unsuitable for temperature-dependent measurements due to the limited availability of defect-free regions. Finally, the accessible temperature window of the instrument (approximately 150–450 K) further constrains material selection. Single crystals of the SCO complex $[\text{Fe}_{0.89}\text{Zn}_{0.11}(\text{bpp})_2](\text{BF}_4)_2$ (bpp = 2,6-bis{pyrazol-1-yl}pyridine) [34-35] were identified as meeting all these requirements.

Experimental

All nanoindentation measurements in this work were performed using a Bruker Hysitron TI 980 TriboIndenter equipped with a three-sided pyramidal diamond tip, the so-called Berkovich indenter. For variable temperature measurements we used the xSol Cryo environmental stage, which enables measurements below room temperature under a protective dry nitrogen atmosphere. The crystals were rigidly fixed on a metallic sample holder using an epoxy glue. Indent centers were spaced typically by ten times the maximum penetration depth to avoid interaction between plastic zones. Before data acquisition, the instrument response was verified and calibrated. In brief, thermal drift was quantified by holding the tip in light contact (2 μN) and monitoring the depth change over a short dwell; the recorded displacement was subsequently corrected using the measured drift rate. To limit time-dependent effects at the onset of unloading, a short hold at the maximum load was included in all protocols. The machine compliance was obtained on fused quartz from stiffness-load series and was accounted for in all stiffness values. The indenter area function $A(h_c)$ was calibrated on a standard fused quartz sample. After indentation the data were corrected for the initial offset from the specimen's free surface.

For data collection, we used the partial unloading method. In this approach, a small load is applied by the nanoindenter, followed by a partial unloading. Subsequently, a slightly higher load is applied and withdrawn, and this cycle is repeated for a predetermined number of steps as shown in Figure 1c. For every partial unloading event, the contact stiffness is extracted from the slope of the initial unloading curve, and the corresponding hardness and reduced modulus

are calculated at that specific contact depth. By repeating this process for all unloading segments, a depth profile of hardness and modulus can be obtained. Indeed, experimental nanoindentation results frequently exhibit variations in these properties with penetration depth, for example due to surface topography, which can be detected and discarded thanks to the partial unloading approach [34-35]. To further increase the reliability of the data acquisition, in-situ surface topography imaging was performed using the indenter tip before and after each indentation experiment (Figure 1d). Pre-scan images were used to select flat, defect-free regions. Post-scan images were used to inspect residual impressions. Tests exhibiting unsuitable topography or anomalous imprint morphologies were excluded from analysis. Importantly for us, in-situ surface imaging turned out indispensable to achieve a homogeneous probe-sample thermalization during variable temperature indentation. In fact, when the probe is retracted from the cold (or hot) surface its temperature changes drastically. On the other hand, it is not possible to maintain the probe in contact with the surface when the temperature is changed, because the thermal expansion/contraction can lead to the damage of the very fragile probe/transducer system. However, the piezoscanner allows us to withdraw the probe only to a slight extent, which is safe for the probe, but in the same time its temperature does not change appreciably. The typical procedure we used for variable temperature measurements consist of (1) bringing the probe in contact of the surface using a small force (ca. 1 μ N) to acquire a pre-scan of the surface, (2) thermal drift test, (3) indentation of the surface in partial unload mode, (4) post-scan surface imaging, (5) withdrawing the probe by 50 μ m, (6) changing the temperature by a small step and (7) waiting for temperature stabilization ($< \pm 0.1$ K). This approach allowed us to achieve controlled temperature indentation with temperature steps as small as 1 K and temperature overshoot less than 0.5 K.

Results and discussion

The compound investigated in this study belongs to the family of mixed-metal molecular spin-crossover complexes with the general formula $[\text{Fe}_z\text{Zn}_{1-z}(\text{bpp})_2](\text{BF}_4)_2$ (Figure 2a). Synthesis and characterization of single crystals with different Fe/Zn ratios were reported in refs. [34-35]. All members of this family crystallize in the monoclinic $P2_1$ space group and the crystal symmetry remains unchanged during the spin transition. The SCO in non-diluted ($z=1$), bulk single crystals is of first-order. It occurs in a very abrupt manner near 262 K with a small (ca. 1.5 K) hysteresis loop. The substitution of Fe(II) by Zn(II) acts as an isostructural dilution, since Zn(II) is a non-magnetic ion that does not participate in the spin transition and therefore reduces the cooperativity of the SCO, which becomes more and more gradual with decreasing values of z . Since the radius of the Zn^{2+} ion (74 pm) is comparable with that of the HS Fe^{2+} ion (78 pm) and much higher than that of the LS Fe^{2+} ion (61 pm), increasing Zn content stabilizes the HS state and shifts therefore the transition to lower temperatures (Figure 2b). Importantly for us, the size and the quality of the crystals also increases with increasing Zn content. The millimeter sized crystals exhibit a plate-like crystal habit, whose largest faces could be assigned to the (001) crystallographic plane using an X-ray diffractometer (Figure 2c). While the surface of the crystals of the pure iron complex was not sufficiently smooth for repeated indentation tests, the single-crystals of compound $[\text{Fe}_{0.89}\text{Zn}_{0.11}(\text{bpp})_2](\text{BF}_4)_2$ (**1**) turned out to be well adapted for indentation, with a large, smooth and planar crystalline face. This composition exhibits still an abrupt, discontinuous spin transition occurring at approximately 251 K, with a tiny hysteresis loop of ca. 0.2 $^{\circ}\text{C}$ width. The first-order nature of the transition is clearly seen in optical

photographs taken across the spin transition for two different sized crystals. As shown in Figure 2d, smaller crystals transform in a temperature interval of less than 1 K, whereas larger crystals show co-existence of the two spin states within a temperature interval of ca. 2-3 K, due to non-uniform thermalization in the cryostage of the microscope.

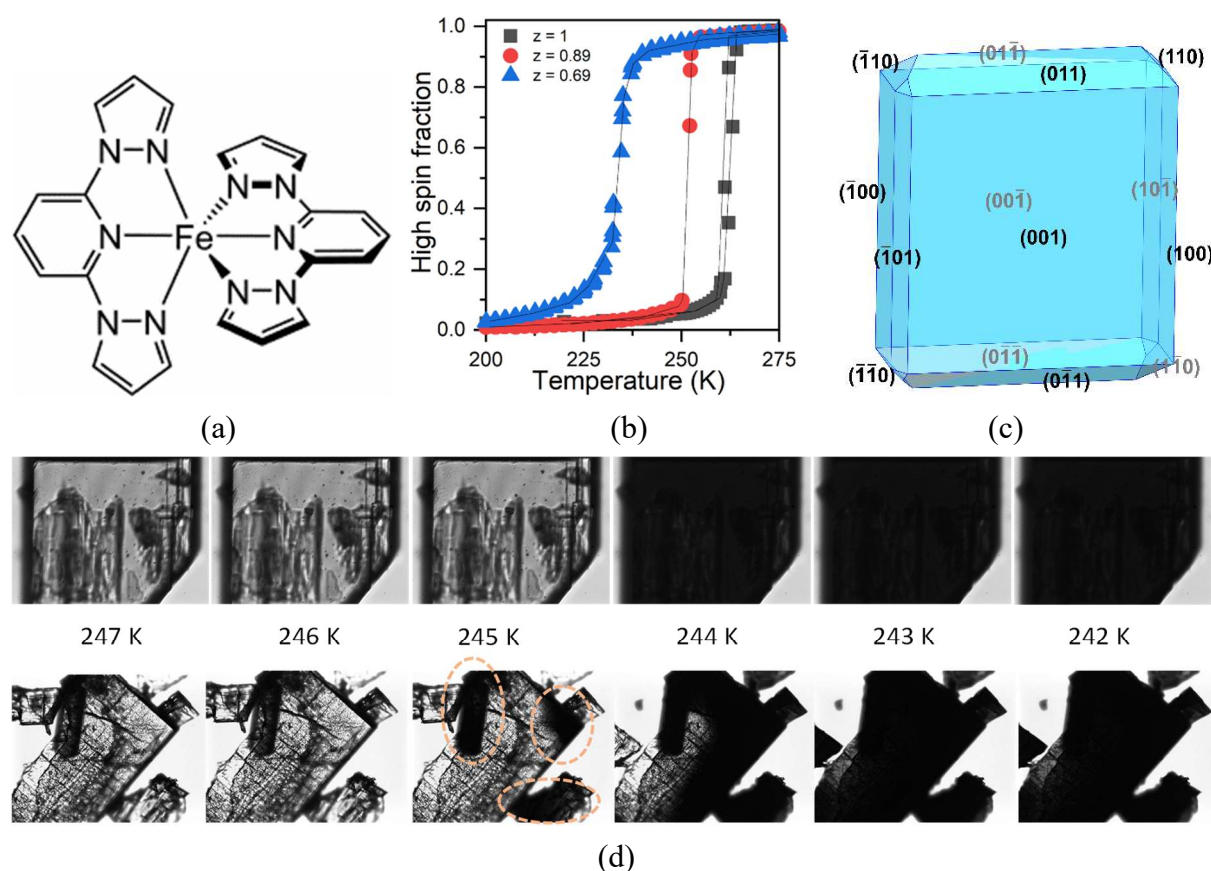


Fig. 2. (a) Chemical structure of the [Fe(bpp)₂]²⁺ complex. (b) High-spin fraction versus temperature for the series [Fe_zZn_{1-z}(bpp)₂](BF₄)₂ ($z = 1, 0.89, 0.69$) obtained from magnetic susceptibility measurements [35], (c) face indexing of a crystal with $z = 0.5$, and (d) optical microscopy photographs acquired in transmission mode (540 nm) upon cooling through the spin transition by steps of 1 K for two crystals of [Fe_{0.89}Zn_{0.11}(bpp)₂](BF₄)₂. Image sizes are 0.18×0.134 mm² (top row) and 1.8×1.34 mm² (bottom row). Orange ellipses show the nucleation of LS domains.

Figures 3a-3b present photos of one of the studied single crystals of compound 1, as observed using the in-situ optical microscope of the nanoindenter. The crystal exhibits a large, flat surface, providing a suitable area for nanoindentation measurements. Overall, the surface appears homogeneous across wide regions. On the other hand, numerous small surface imperfections are visible, which are likely associated with natural crystal growth or subtle surface texture. The precise positions of the indentation sites were therefore systematically verified using the in-situ surface imaging. As an example, Figure 3c shows an image taken from an area of this crystal, illustrating the smooth surface topography and the occurrence of small “pyramid-like” surface features consistent with the optical observations. The indents were placed in “clean” areas away from the larger features. Figure 3d presents an image acquired after indentation, showing a proper indent. A representative load–displacement curve obtained with the partial unloading method is shown in Figure 3e. The smooth and continuous character of the curves indicates stable contact and good reproducibility of the mechanical response. Figure 3f shows the extracted reduced-modulus profiles as a function of indentation depth,

showing a broad region from which intrinsic material properties can be extracted. These figures also allow to appreciate the typical uncertainty (ca. $\pm 10\%$) when probing different zones on the same crystal facet. To test the internal consistency of the indentation data, we have made room temperature indentation tests on crystals with different Fe-Zn ratios. Within the experimental uncertainty, the data, compiled in the inset of Figure 3f, reveal no substantial difference in the mechanical properties of these crystals. This can be readily understood by taking into account the very similar ionic radii of Zn^{2+} and high spin Fe^{2+} and the isostructural nature of the series.

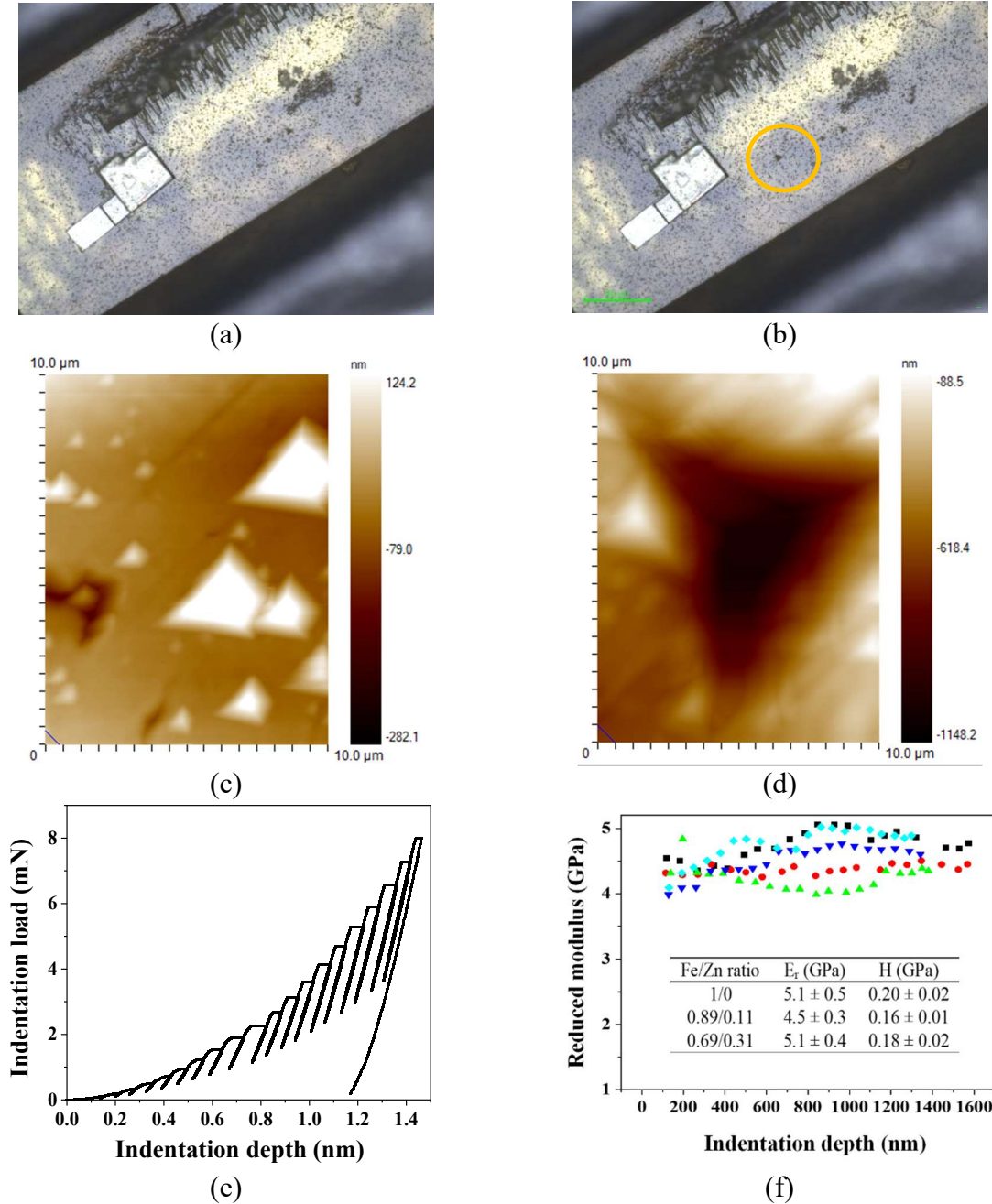


Fig. 3. Optical image of an $[\text{Fe}_{0.89}\text{Zn}_{0.11}(\text{bpp})_2](\text{BF}_4)_2$ single crystal before (a) and after (b) nanoindentation. The indent is shown by the orange circle. Surface topography image of the same crystal obtained in-situ before (c) and after (d) nanoindentation. e) Representative load-displacement curve of a crystal of $[\text{Fe}_{0.89}\text{Zn}_{0.11}(\text{bpp})_2](\text{BF}_4)_2$ and (f) the extracted typical room temperature depth profiles of the reduced modulus. Different colors indicate data acquired at different locations of the crystal. The inset shows the average values of the reduced modulus and hardness for $[\text{Fe}_z\text{Zn}_{1-z}(\text{bpp})_2](\text{BF}_4)_2$ crystals with different degrees of Zn doping.

For the variable temperature studies we continued with compound **1**, characterized by 11 % Zn doping. Using the partial unloading procedure shown in Figure 1c, a first temperature-dependent measurement series was performed on a crystal of **1** from 296 K to 203 K with 5 K intervals. Reduced modulus and hardness extracted from the plateau of each depth profile are reported in Figures 4a-4b, respectively. At 296 K, where the material is fully in the HS state, the reduced modulus is approximately 4.6 ± 0.1 GPa. At lower temperatures, the modulus progressively decreases to reach a value of 3.3 ± 0.1 GPa at 253 K. This ‘premonitory’ softening when approaching the transition point might be an indication of enhanced spin-state fluctuations [13]. Most remarkably, a pronounced softening is observed near 248 K, where a minimum value of about 2.0 ± 0.1 GPa is observed. Below this temperature, the modulus increases swiftly to 4.0 ± 0.7 GPa at 243 K, reaching gradually 7.8 ± 0.4 GPa at 203 K. The hardness displays much less variation than the reduced modulus with values around 0.18 ± 0.02 GPa at most of the measurement points, except for a notable decrease near 248 K to about 0.110 ± 0.004 GPa. Since compound **1** is known to display an abrupt spin transition near this temperature value (depending on the accuracy of the temperature measurement), it is tempting to associate the observed softening of the modulus and the hardness with the SCO phenomenon.

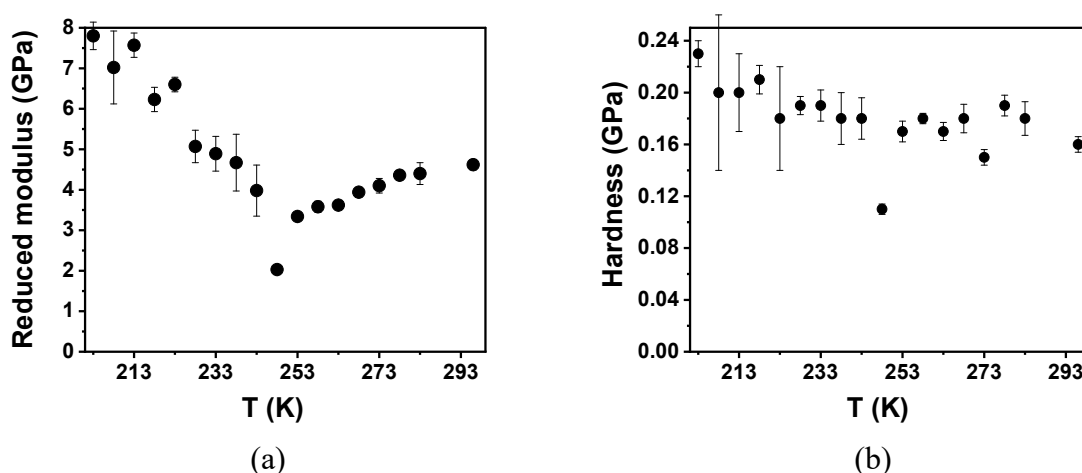


Fig. 4. Temperature dependence of (a) the reduced modulus and (b) the hardness of a $[\text{Fe}_{0.89}\text{Zn}_{0.11}(\text{bpp})_2](\text{BF}_4)_2$ crystal obtained from partial-unloading nanoindentation measurements upon cooling. (Indiscernible error bars are smaller than the font size.)

In the next step, a second crystal of **1** was studied through three successive measurement series using the same load function and data analysis. The results of these experiments are summarized in Figure 5. Due to technical constraints, we could only run indentation tests at low temperatures for a limited duration (typically for 8-12 consecutive hours). For this reason, each series is limited to ca. 10 - 15 temperature points. In a first experiment, the temperature was swept from 263 K to 248 K with 5 K steps. The top panel of Figure 5a shows the reduced modulus as a function of temperature. In this run, the modulus softening was not resolved and the modulus value remained within the same interval (4 ± 1 GPa) through the entire temperature range. To identify why the softening was not captured, a second experiment was performed with finer sampling, wherein the temperature was swept from 263 K to 243 K in 2 K decrements. As shown in the middle panel of Figure 5a, the reduced modulus slightly decreased from 4.1 ± 0.1 GPa to 3.1 ± 0.1 GPa when cooling the sample from 263 K to 251 K, then it exhibited a sharp

drop to reach 1.8 ± 0.1 GPa at 249 K, followed by a sharp increase to 6.0 ± 0.1 GPa at 247 K with an apparent stabilization at ca. 6.9 ± 0.2 GPa around 243 K. These results place the elastic anomaly at 249 K in this crystal. The first series did not resolve the anomaly because the coarse 5 °C step excluded the sharp transition point.

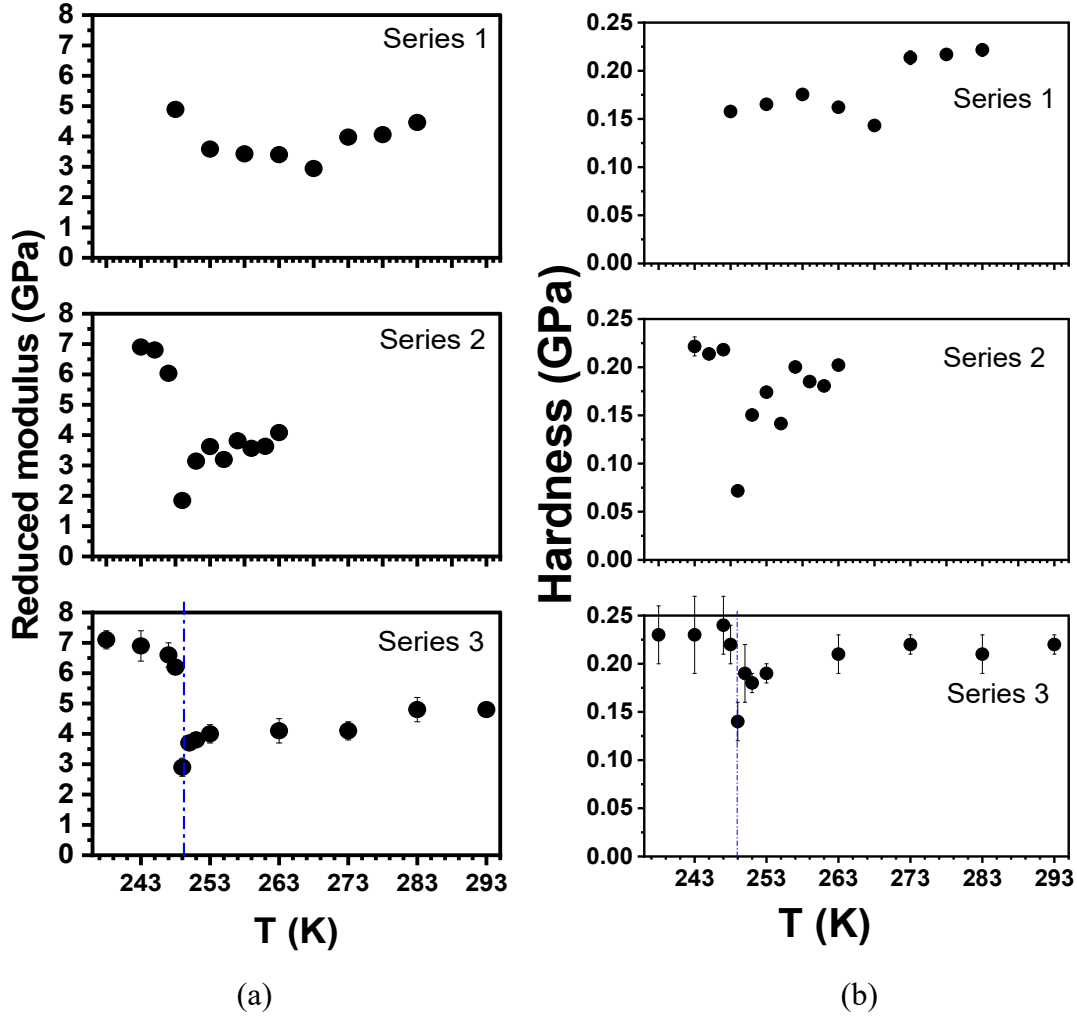


Fig. 5. Temperature dependence of (a) the reduced modulus and (b) the hardness of a second crystal of $[\text{Fe}_{0.89}\text{Zn}_{0.11}(\text{bpp})_2](\text{BF}_4)_2$ obtained from partial-unloading nanoindentation measurements upon cooling for three successive measurement series. (Indiscernible error bars are smaller than the font size.)

A third series of measurements was then conducted to further refine the transition temperature and to validate the previous observation. This time, the temperature was varied from 293 K to 238 K during cooling, with coarse steps far from the transition and 1 K decrements near the transition point. The bottom panel of [Figure 5a](#) reports the results of this test. Similar to the previous test, upon cooling the crystal from 293 K to 250 K, E_r decreased gradually from 4.8 ± 0.2 to 3.7 ± 0.2 GPa. Then, at exactly 249 K, it dropped sharply to 2.9 ± 0.3 GPa, followed by a sharp increase to 6.2 ± 0.2 GPa at 248 K to reach a stable value of 7.0 ± 0.3 GPa below 243 K. Taken together, these variable-temperature indentation experiments demonstrate a sharp, reproducible elastic anomaly confined to a narrow interval centered at 249 K. Unmistakably, the hardness exhibits the same anomaly than the reduced modulus, with a marked softening from ca. 0.18 GPa to 0.07 GPa at 249 K (see [Figure 5b](#)). However, contrary to the modulus, far from this point, the hardness shows much less difference between the high spin and low spin

phases, the latter being only slightly harder. At this point, it is also instructive to compare the measured data for the two different crystals, which are shown in [Figures 4-5](#). The absolute values of the modulus and hardness as well as the general features of their temperature-dependence are similar for the two crystals. Most importantly, in both cases a sharp and localized softening can be depicted, though at slightly different temperatures (248 vs. 249 K). Some other differences are also observed. In particular, the variation of the modulus in the LS state is more gradual for the first crystal. This difference might be related to a slightly different sample orientation (vs. the indenter axis) and/or to different local compositions. Indeed, one cannot exclude small local variations of the Zn doping level in the crystals, which can give rise to different responses to the temperature change.

Regarding the origin of the softening at the transition point, a first indication comes from the closer inspection of the load-displacement data. As shown in [Figure 6a](#), below and above the “softening point”, changing the temperature brings only small changes to the load-displacement curves. However, the data recorded at the softening point (249 K) strongly deviates from the rest of the series, not only because of the higher indentation depth (i.e. softening), but most remarkably by the shape of the curves, displaying broad “loops”. Indeed, when zooming on the curves recorded at 247 K and 249 K ([Figure 6b](#)), one can see that at 247 K the partial unloading and subsequent loading curves are almost superimposed. On the contrary, at 249 K a spectacular hysteresis appears between the two curves. This phenomenon probably arises from multiple physical contributions (creep, spin-state relaxation, ...), but in any case, it denotes the occurrence of prominent time-dependent phenomena and associated energy dissipation. Similar to other types of phase transitions, such time-dependent mechanical phenomena can be linked to classical order-parameter relaxation effects: the delayed response of the spin state of the system to the mechanical stress results in the relaxation of the modulus and associated energy dissipation [[13](#), [38-39](#)]. In the case of $[\text{Fe}_{0.89}\text{Zn}_{0.11}(\text{bpp})_2](\text{BF}_4)_2$ crystals, one expects a particularly strong coupling between the SCO phenomenon and the mechanical properties along the crystallographic *c*-axis. As discussed in ref. [[40](#)], the $[\text{M}(\text{bpp})_2]^{2+}$ cations form closely packed (001) layers through π - π interactions and C...H... π contacts between pyrazolyl rings of neighbor cations. Interestingly, the LS to HS transition in **1** gives rise a small contraction in the *ab* plane with values of $\Delta a/a = -0.24\%$ and $\Delta b/b = -0.61\%$. Such counter-intuitive behavior of lattice parameters is not unusual in SCO materials and it is largely offset by the expansion of the *c*-axis ($\Delta c/c = +2.34\%$), which ensures the expected positive volume strain ($\Delta V/V = +1.9\%$). In fact, the along the 001 direction, the $[\text{M}(\text{bpp})_2]^{2+}$ layers are stacked rather loosely and separated by the BF_4^- counterions. This specific structural arrangement is clearly reflected in the reported thermal expansion behavior of the $[\text{Fe}_z\text{Zn}_{1-z}(\text{bpp})_2](\text{BF}_4)_2$ crystals, which show a large and strongly spin-state dependent coefficient of thermal expansion (CTE) normal to the *ab* plane, and a much smaller in-plane CTE, which is also less spin-state sensitive [[34-35](#)]. In our indentation experiments the indentation axis being (roughly) aligned with the *c*-axis of the crystal, one can indeed expect a strong deformation to occur due to the mechanical stress-induced spin state relaxation. As a result, near the transition point the material exhibits virtually no resistance to the applied load and strong mechanical dissipation occurs. On the other hand, the observation of a strongly increased “background” elastic modulus in the LS state (ca. 7.0 GPa vs. 4.5 GPa in the HS state) is not a relaxation effect. Rather, it stems simply from the fact that the contracted lattice is also less compressible, in agreement with Birch’s law [[41](#)].

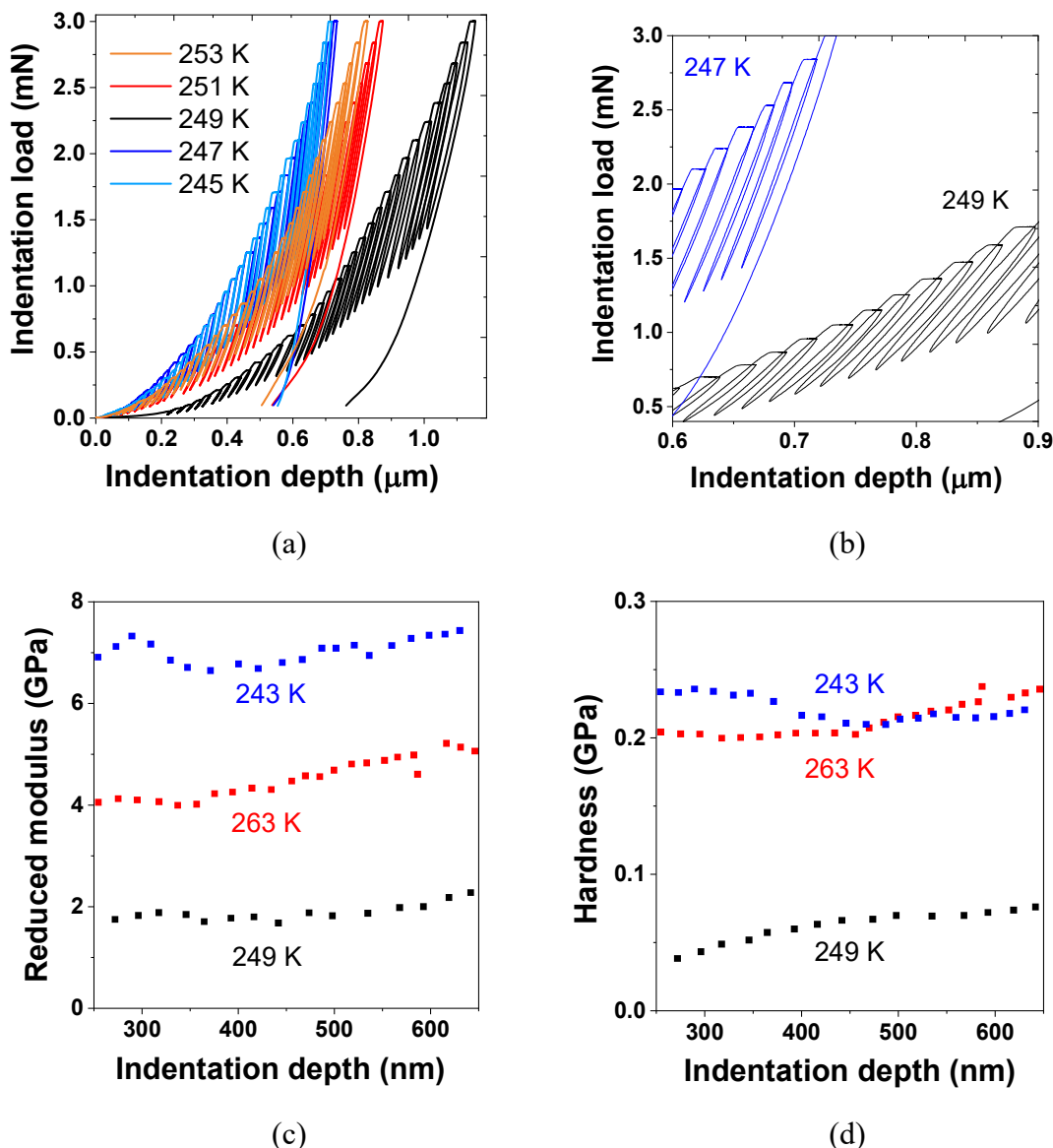


Fig. 6. (a) Representative load–displacement curves of a crystal of $[\text{Fe}_{0.89}\text{Zn}_{0.11}(\text{bpp})_2](\text{BF}_4)_2$ below (245, 247 K), above (251, 253 K) and at the “softening point” (249 K). (b) Zoom on the curves at 247 K and 249 K. Indentation depth dependence of the (c) reduced modulus and (d) hardness at selected temperatures for the measurement “series 2” shown in Figure 5. (The data at shallow indentation depths are prone to surface effects and therefore they have been discarded.)

An important question here concerns the nature of the spin-state relaxation induced by the indenter tip. One may assume that it should be a genuine phase transition, which proceeds via nucleation and growth, similar to the thermally-induced SCO in **1** shown in Figure 1d. However, the indentation depth profiles recorded at the softening point at 249 K (Figure 6c-6d) seem to contradict this idea. In the case of a nucleation and growth process, as the indentation load increases, one should expect a very significant increase of the modulus. The fact that the extracted modulus is basically constant (within the experimental uncertainty) through a broad range of partial unloading data points suggests that the spin state relaxation is a fast and reversible process. We can therefore suggest that the mechanical stress results in the transformation of isolated molecules (or small clusters) without forming a structured nucleus of the LS phase. The fact that the indenter does not seem to be able to trigger the phase transition must be linked to the large difference between the size of the crystal (mm^3 scale) and the

indentation volume (μm^3 scale). Indentation studies on different sized crystals appear thus potentially very interesting.

Finally, one should also notice that the spin state dependence of the hardness is significantly different from that of the modulus (see [Figures 4-6](#)). Actually, both hardness and modulus show a strong softening at the transition point. On the other hand, the pronounced stepwise increase of the elastic modulus when going from the HS to the LS state is much less seen in the hardness data. This finding is somewhat surprising because the elastic properties ($\sim$ modulus) and plastic deformation ($\sim$ hardness) are usually both related to the lattice stiffness. However, it is important to remind that the microscopic physical mechanisms governing elasticity ($\sim$ intra- and inter-molecular bond stretching) and plastic behavior (dislocation formation and movement) are obviously rather different and therefore they are not always correlated [42]. Whatever its physical origin, the sizeable change of the hardness over modulus (H/E) ratio denotes significantly different tribological properties of the HS and LS phases, such as wear resistance or contact brittleness [43], which might be an interesting, non-anticipated property for the development of functional coatings with adaptive/tunable contact behavior. Further work will be, however, necessary to establish whether this substantial decoupling of the hardness from the lattice stiffness across the spin transition is a general property of SCO materials or a specificity of the crystal studied in the present work.

Conclusions

In summary, we investigated the mechanical properties of single crystals of the spin-crossover complex $[\text{Fe}_{0.89}\text{Zn}_{0.11}(\text{bpp})_2](\text{BF}_4)_2$ by means of variable-temperature nanoindentation, with the aim of probing the evolution of elastic modulus and hardness across the thermally induced spin transition. A significant methodological outcome of this study is the establishment of a reliable protocol for low-temperature nanoindentation of sub-mm sized molecular crystals. Particular attention was devoted to crystal growth, optimization of indentation parameters, and careful control of the probe-sample thermal equilibrium. These developments enabled reproducible measurements with temperature steps as small as 1 K in the vicinity of the transition. The measurements reveal a sharp and highly reproducible elastic anomaly confined to a very narrow temperature interval around 249 K. This anomaly is characterized by: (i) a pronounced minimum in the reduced modulus at the transition temperature, (ii) a subsequent abrupt, step-like stiffening upon transformation from the HS to the LS state, and (iii) a concomitant dip in hardness. The elastic softening is attributed to finite-rate relaxation of the spin state of the molecules toward its new equilibrium under applied mechanical stress. Consistent with this interpretation, large hysteresis loops appear in the load-displacement curves at the transition temperature, highlighting the importance of time-dependent processes and associated energy dissipation. While both modulus and hardness exhibit strong softening at the transition point, their behavior away from the transition differs markedly. The step-like renormalization of the elastic modulus (nearly twofold increase in the LS state) is not mirrored by a comparable increase in hardness.

Overall, these results demonstrate that variable-temperature nanoindentation is a powerful and versatile technique for quantifying elastic anomalies associated with spin-crossover and (in general) phase transition phenomena. The method effectively bridges the gap between macroscopic mechanical testing, which requires large samples, and spectroscopic approaches that probe elastic constants at high frequencies. Beyond their fundamental significance, these

findings are directly relevant to the mechanical performance of SCO-based devices, particularly in relation to load-bearing capacity and the efficiency of thermo-mechanical energy conversion. Future work should aim to integrate these experimental observations into a comprehensive theoretical framework and to further exploit the capabilities of nanoindentation, including the investigation of elastic anisotropy, frequency-dependent response, and additional mechanical and tribological properties such as fracture toughness, adhesion, and wear.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

The data supporting this article are available from the authors upon reasonable request.

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