The kinetics features of a thermal spin transition characterized by optical microscopy on the example of [Fe(bbtr)_3][(ClO_4)_2] single crystals: Size effect and mechanical instability

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A B S T R A C T
We investigated by optical microscopy the thermal spin transition in single crystals of [Fe(bbtr)_3][(ClO_4)_2] (bbtr = 1,4-di(1,2,3-triazol-1-yl)butane). The growth of the low-spin phase was observed for different crystal orientations and sizes. The process always started from a corner of the crystal but its further development depended on the size, shape and thermal history of the crystal. In crystals of smaller size, under isothermal conditions, the low-spin phase developed in a continuous way, through the propagation of a rather well defined transformation front, with a higher propagation velocity inside the planes perpendicular to the c axis. In larger crystals the spontaneous occurrence of inhomogeneous stresses led to a stepwise propagation process.

1. Introduction
Spin transition solids (see recent review [1]) provide beautiful examples of first order solid-state phase transitions, the thermal hysteresis width of which can reach ~100 K. Some of these compounds have a hysteresis loop centred around room temperature and are promising for potential applications in information storage [2] and/or optical switching [3]. Usually the order parameter associated with the spin transition is the high-spin fraction, n_HS, that is the fraction of molecules which are in the high-spin state. Convenient n_HS measurements can be based on physical quantities (magnetic susceptibility, metal–ligand distance, specific heat) or spectroscopic data (optical absorption, diffuse reflectance, Mössbauer, Raman) which can be accurately determined in the high-spin (HS) and low-spin (LS) states. Like any first-order transition, the spin transition takes place through the nucleation and growth of domains coined Like-Spin Domains (LSD) [4]. Such LSDs have been evidenced by X-ray diffraction on single crystals for both thermo-induced [5] and photo-induced [6] spin transitions. LSDs are also involved in the photo-induced phase separation process

[7,8]. The spatiotemporal aspects of the spin transition were only recently considered, so far by means of optical microscopy [9,10], which clearly showed the propagation of a phase boundary [11,12]. Such experimental information promoted modelling work aiming to determine the location of nucleation centres at the thermal [13,14] and photo-induced [15] transitions, or to establish scaling laws for the light-induced phase separation [16].

Here we report on some selected results obtained through the preparation of the thesis of Chong [12], completed by a recent investigation of crystals of smaller size. We investigated single crystals of the compound [Fe(bbtr)_3][(ClO_4)_2] (bbtr = 1,4-di(1,2,3-triazol-1-yl)butane), here abbreviated Fe(bbtr), which shows an abrupt thermal spin transition and thermal hysteresis with T_c = 113 K and T_f = 95–103 K depending upon the history of the crystal. This compound [17] can be considered as the polymer analogue of [Fe(ptz)_6][BF_4]_2 (abbreviated Fe(ptz)) in the following, ptz = 1-propyltetrazole), which we recently investigated by optical microscopy [10]. In both systems, the spin transition is coupled to a structural transition between an ordered high-temperature structure R3 and a disordered low-temperature structure, well documented in the case of Fe(ptz) [18]. Using a colorimetric method we could follow separately the electronic and structural aspects of the transition by optical microscopy [10]. The recent study of Fe(bbtr) single crystals by optical absorption [19] aimed to elucidate the interplay between the structural and electronic transformations, and evidenced an unusually important scattering of

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light by the disordered phase. It also reported the stepwise HS → LS relaxation curves in the vicinity of the thermal hysteresis, which are reproduced in Figure SM1 (Supplementary material), with an intriguing character, which prompted the present study by means of optical microscopy.

2. Experimental part

The crystals investigated here were prepared by Bronisz for previous work using optical absorption spectroscopy [19,20]. Crystals had a prismatic shape with edges parallel to the c axis of the R3 structure. We checked by the crossed polarizer technique that c is also the optical axis of the system. The microscope setup and its cryogenic adaptation (helium tight cell) were already described in Ref. [10]. The optical resolution, after image digitalization was estimated to be ~2–3 μm. Temperature was very homogeneous and stable. The crystals were not glued to the optical window in order to avoid any stress. Because of this, crystals tended to move around or even to jump inside the cell during the transition.

In the microscope sample cell, we systematically set couples of crystals with the two possible orientations, that is, with the c axis of the R3 structure along the microscope axis z (‘top view’) or in a perpendicular orientation (‘side view’), see Table 1. The dimensions of the crystals are also reported in Table 1. The data relative to crystals A, B originate from Chong’s PhD Thesis [12]. Those for crystals C, D were obtained more recently. When observed between crossed polarizers, in side view, all crystals exhibited beautiful extinction for c parallel to either of the two polarizers, which demonstrated their excellent structural quality, see Figure SM2. In contrast, the crystals in top view, which should show extinction irrespective of the orientation, exhibited a sizeable scattering of light, which was uniform and also irrespective of the orientation (Figure SM2). This anisotropic scattering effect revealed the presence of stacking faults of the 2D polymeric planes. The quantitative data are expressed in terms of optical densities (ODs) as in previous work [9,10].

Thanks to the similarity of the optical absorption spectra of the compounds Fe(bbtr) and Fe(ptz), we could take advantage of the colorimetric method introduced in Ref. [9]: the absence of electronic absorption bands in the red and blue spectral ranges lead to assign the red and blue ODs to scattering of light, due either to the disordered phase or to inhomogeneous internal stresses; in contrast, the green OD could be used to monitor the spin transformation. This method enabled us to elucidate the spatiotemporal aspects of the interplay between structural and electronic transformations at the thermal transition of Fe(ptz) single crystals [10] and will be used here on Fe(bbtr).

3. Results and discussion

Crystals A, B were placed together in the sample cell and slowly cooled down to the temperature range of the thermal transition (0.5 K/min below 120 K). We show in Figures 1 and 2 the most representative images obtained during the first cooling stage. Both crystals displayed a step-wise and non-homogeneous HS → LS transformation. The coexistence between HS and LS macroscopic regions over a ~15 K wide temperature interval was observed in both crystals. The transition temperature 98 K associated with the first step of the transition is in rough agreement with the value reported in the literature, that is, 102 K [19,20] on the basis of the optical absorption of single crystals of smaller size. The further evolution till ~82 K can be described as the trapping of the HS state in stressed regions of the crystals, according to the well-known pressure effect (see for instance [21]). We speculate that such mechanical stresses could be generated by the volume change associated with the spin transition. Obviously, the larger the crystals, the larger the resulting stresses. The non-homogeneous character of the stresses reveals the presence of a mechanical instability above some critical size of the crystal. These speculations are supported by the more recent investigation of smaller crystals, reported in the following, which made possible the monitoring of the HS → LS transition in absence of the said mechanical instability.

A couple of fresh crystals of smaller size, C, D, were inserted into the sample cell, and slowly cooled down from 120 K at 0.2 K/min. At 98.07 K the transition of crystal C started and we immediately stabilized temperature at 98 K in order to observe the isothermal evolution of the crystals, which was completed within a relatively short time, ~25 s and 100 s for crystals C, D respectively. Selected images are shown in Figures 3 and 4, revealing that the transition indeed can proceed in a single step in smaller crystals.

The top view (Figure 3) shows a rapid propagation starting from a corner of the thin side of the crystal. Then in the small crystal, the HS → LS transition took place with a rather smooth propagation front, the shape of which was circular at the beginning, but evolved in the following, presumably governed by the propagation limit conditions, that is, the edges of the crystal. The propagation velocity of the front perpendicular to the crystal c-axis was determined to be ~9 μm/s during most of the transformation but increasing noticeably at the end of the process. This shows that the propaga-

Table 1

<table>
<thead>
<tr>
<th>Label</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>~100 μm</td>
<td>175 μm</td>
<td>135–190 μm</td>
<td>200 μm</td>
</tr>
<tr>
<td>Ext. diameter/cross-section</td>
<td>430 μm</td>
<td>~320 × ~160 μm</td>
<td>320 μm</td>
<td>~295 × 200 μm</td>
</tr>
<tr>
<td>Top view</td>
<td>Side view</td>
<td>Thickness was inferred from ODs</td>
<td>After thermal cycle</td>
<td></td>
</tr>
</tbody>
</table>

Physical description of the crystals, derived from their top and side views. Thickness and cross section refer to the c axis. Images were taken in bright field transmission geometry without any polarizers.
tion velocity can be correlated to the shape of the transformation front, in other words it is governed by the limit conditions. A detailed study of these shape effects would require improving the time resolution of the investigation. This study will be undertaken as soon as possible and is expected to provide insight into the nucleation and growth mechanism, which we recently showed to be a multi-scale process [22].

The side view, Figure 4, showed a rather a more diffuse start at the bottom of the crystal, nevertheless followed by a well-defined linear transformation front, indicating an LS/HS interface parallel to the microscope axis. The propagation velocity was determined as \( \sim 2 \, \mu \text{m/s} \). The orientation of the transformation front, at \( \sim 77^\circ \) from the \( c \) axis, is in excellent agreement with the ratio of the parallel and perpendicular components, respectively determined from the side and top views: \( \sqrt{\frac{v(\parallel c)}{v(\perp c)}} \sim 2/9 \sim 1/\tan 77^\circ = 0.23 \). Such a large anisotropy of the propagation velocity obviously implies an anisotropic character of the elastic (or visco-elastic) properties of the compound, in agreement with its 2D polymeric nature.

At last, we could elucidate the stepwise character of the kinetic curves, see Figure SM1, which initially motivated the present study, by repeating the thermal cycles. Indeed, in all cases, such repeated cycles created irreversible damage in the crystals, including both visible features such as cracks or self-cleavage effects and microscopic features, responsible for an irreversible increase in the red and blue ODs, assigned to diffuse scattering of light by microstructures. Such damage obviously resulted from the mechanical stresses due to the volume change associated with the spin crossover. The possible role of the structural transition coupled to the spin transformation [19,20] remains to be investigated in detail by the simultaneous recording of bright field and crossed polarizer geometry, which is planned. We show in Figure 5 selected top views of crystal C at 98 K, during the second isother-
mal transition at 98 K, that is, after the second cooling at 0.2 K/min from 120 K. The HS → LS transition proceeded in a more complex way, starting from several points on the contour of the crystal. We measured the three ODs in average over the images and obtained the stepped character reported in Figure 6. The steps can be assigned to the transformations of separate pieces of the crystal, which are clearly visible on the final views of aged crystals, see Figure SM3. We finally interpret the stepwise character of the data reported in Figure SM1 as due to the progressive damage of the crystal along the following sequence: 120 K → 101.1 K → 120 K → 102.0 K → 120 K → 103.0 K → 120 K → 102.5 K → 120 K.

The first kinetic curve (101.1 K) had no visible step, while further curves exhibited an increasing number of steps associated with the successive transitions of the various pieces of the aged crystal. In addition, the kinetic data of Figure 6 confirm the previous statement (based on Figures 1 and 2) that the nucleation and growth process is influenced by the presence of internal stresses.

According to [10] the irreversible increase of all values from run (1) to run (2) is assigned to scattering of light by micro-sized and

Figure 4. Crystal D, side view, during HS → LS isothermal transformation at 98 K (first cooling). Supplementary Material: Video 4.

Figure 5. Crystal C, top view, during repeated HS → LS isothermal transformation at 98 K. Supplementary Material: Video 5.

Figure 6. The time dependence of the ODs measured in average on crystal C during the first and second isothermal transformations at 98 K.
extended defects, in agreement with the observed rise of the baseline of optical absorption spectra [19].

4. Conclusion

Thanks to optical microscope images we followed the propagation of the spin transition in Fe(bbtr) single crystals. We evidenced size effects associated with the onset of inhomogeneous stresses in the crystals, leading to mechanical instability in the case of larger crystals. The propagation velocity was determined and its anisotropic character revealed (slower along the packing direction of the 2D polymeric planes). Shape effects were also evidenced. The stepwise isothermal relaxation reported in Ref. [19] was assigned to crystal aging due to the development of inhomogeneous stresses at the transition. The presence of such stresses might also explain the stepped character of the photo-excitation curve reported in [23]. We now undertake the detailed investigation of the spatio-temporal aspects, in order to document the fascinating problem of the mechanical instability and set up realistic models involving the rheological response of the materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2011.01.041.

References