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Satellite reflection study of the incommensurate phase in $\left(\text{N}\left(\text{CH}_3\right)_4\right)_2\text{ZnCl}_4$ crystal by means of real-time X-ray synchrotron topography

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Résumé. — Une étude de monocristaux de $\left(\text{N}\left(\text{CH}_3\right)_4\right)_2\text{ZnCl}_4$ au rayonnement Synchrotron a permis de suivre, en temps réel, l’évolution d’une réflexion satellite au-dessus de la transition de blocage. Des effets de relaxation associés à la distribution des défauts ont été mis en évidence lors de cycles thermiques.

Abstract. — A real-time X-ray Synchrotron study of $\left(\text{N}\left(\text{CH}_3\right)_4\right)_2\text{ZnCl}_4$ single crystals allows one to follow the evolution of a satellite reflection above the lock-in transition. Thermal cycles give evidence for relaxation effects associated with the defect distribution.

1. Introduction.

It is generally admitted that the formation of intrinsic defects associated with incommensurate phases [1] and their interaction with extrinsic defects play an essential role near the lock-in transition. In particular, they would explain abnormal temperature behaviours such as global hysteresis, memory effects [2-5] and relaxation phenomena associated with the evolution of the satellite rocking curves [6].

Intrinsic linear defects appearing at the lock-in transition have already been observed in nearly perfect tetramethylammonium-tetrachlorozincate ($\text{TMA}_2\text{ZnCl}_4$) single crystals, by means of real-time X-ray Synchrotron Topography, using Bragg reflections [7]. Such defects have been interpreted in terms of deperiodisation lines [1].

In the present study, X-ray Synchrotron Topography has been applied both to Bragg reflections and to satellite reflections. A simultaneous recording of the rocking curves allows the determination of the modulation wave vector corresponding to different regions in the crystal. In order to study the influence of extrinsic defects (such as dislocation lines or radiation defects) on the modulation wave vector, a characteristic sample showing areas of different crystalline quality has been selected.

2. Experimental.

$\text{TMA}_2\text{ZnCl}_4$ single crystals have been grown on a seed, by temperature decrease of a saturated aqueous solution of $\text{N}\left(\text{CH}_3\right)_4\text{Cl}$ and $\text{ZnCl}_2$ in a stoichiometric ratio. Parallel (100) plates (with Pnma notation) are cut out of the crystals and polished down to a thickness of about 0.7 mm.

The experimental set-up consists in a double-diffractometer at LURE-DCI (Orsay, France) used in the $++$ geometry. The first Ge crystal used with the 220 reflection delivers a wide beam of wavelength equal to 0.6 Å and angular divergence of about 30° of arc. X-ray topographs of the second crystal under study, $\text{TMA}_2\text{ZnCl}_4$, are recorded using the 020 Bragg reflection and the $\delta20$ or $\delta20$ satellite reflections. The corresponding rocking curves are recorded as a function of the rotation angle of the sample about the $c$ axis. The value of the modulation wave vector parallel to $a^*$ is deduced from the mean separation between the $\delta20$ or $\delta20$ satellite peak and the 020 Bragg peak. The sample is located in a thermostated cell with a temperature stability better than 0.1 °C.

The phase sequence of $\text{TMA}_2\text{ZnCl}_4$ single crystal is presented as a function of temperature in
Table 1. — Sequence of phases of (TMA)$_2$ZnCl$_4$ versus temperature, under atmospheric pressure.

<table>
<thead>
<tr>
<th>Phase I</th>
<th>23°C</th>
<th>Phase II</th>
<th>7°C</th>
<th>Phase III</th>
<th>3.5°C</th>
<th>Phase IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pnma</td>
<td></td>
<td>Incommensurate</td>
<td>Pn2$_1$a</td>
<td>Commensurate</td>
<td>P2$_1$/n11</td>
<td>Commensurate</td>
</tr>
<tr>
<td>$a = 12.276$ Å</td>
<td></td>
<td>$q = (2/5 - \alpha) a^*$</td>
<td>$q = 2/5 a^*$</td>
<td></td>
<td>$q = 1/3 a^*$</td>
<td></td>
</tr>
<tr>
<td>$b = 8.998$ Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c = 15.541$ Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

table I. Here, we will only discuss the results concerning the incommensurate (II) phase and the lock-in (II-III) transition.

3. Results and discussion.

3.1 ROCKING CURVE AND MODULATION WAVE VECTOR. — The temperature has been decreased from 20°C to 4°C at a rate equal to 0.5°C.min$^{-1}$. Thermal equilibrium has been achieved at various temperatures before recording the rocking curves.

The full width at half maximum (FWHM) of the 020 rocking curve does not significantly vary with the temperature. It remains equal to the instrumental width i.e. 30' of arc (the intrinsic width in the case of a perfect crystal would be equal to 1.3" for the 020 reflection, using the 0.6 Å wavelength). On the opposite, the FWHM of the 820 satellite rocking curve depends on the temperature (Fig. 1). By lowering the temperature, the 820 FWHM increases up to about three times the instrumental width when approaching the lock-in transition; below the transition temperature $T_c$ the 2/5 20 FWHM rapidly decreases over a few tenths of a degree centigrade. The anomalous broadening of the 820 rocking curve observed from 14°C to $T_c$ indicates that the incommensurate wave is severely perturbed. This fact has been reported previously for other compounds such as Rb$_2$ZnCl$_4$ [3] and (NH$_4$)$_2$BeF$_4$ [8]. Since, in our case, the broadening takes place in a rather large temperature range, it could be attributed to a pinning of the modulation by extrinsic defects. Moreover, since no further narrowing of the 820 FWHM has been observed during one hour, one may think that these pinning defects cannot rapidly diffuse through the sample in order to adapt their spatial distribution to the ideal form of the modulation. The values of the modulation wave vector have also been determined as a function of the temperature, during the first cooling process (full line AB, Fig. 2). This curve is in agreement with the observations previously reported [9]. Faint modifications, due to radiation damage, arise for further thermal cycles.

![Fig. 1. — Evolution with the temperature of the full width at half maximum (FWHM) of the 820 satellite rocking curve.](image1)

![Fig. 2. — Variation of the $q$ wave-vector during thermal cycles.](image2)

3.2 KINETIC EFFECTS IN RELATION WITH CRYSTAL-LINE QUALITY. — The sample has then been heated from 5°C to 11°C, at a rate of 0.5°C/min. After waiting the equilibrium at $T_1 = 11°C$ for about twenty minutes, the temperature has been decreased down to $T_2 = 9°C$ at the same rate; the corresponding variation of the modulation wave vector is presented in dashed line (Fig. 2). The satellite rocking curve, at $T_2$, shows two peaks centred at $q_1 = 0.413(5)a^*$ and $q_2 = 0.411(8)a^*$, associated respectively with the equilibrium values of the modulation wave vector at $T_1$ and $T_2$ (Fig. 3a). The maximum intensity of the $q_1$ peak decreases exponentially with time (Fig. 3b) while the maximum intensity of the $q_2$ peak increases; the relaxation time has been estimated to about 100 s.

X-ray topographs associated with each peak have been made. The central part of the sample is in a
Fig. 3 — Visualization of a relaxation effect induced by T decrease. a) Satellite rocking curve, at $T_2$, showing two peaks (the intensity unit is referred to that of the 020 Bragg peak). b) Variation of the $q_1$ peak intensity with time. c-d) X-ray topographs taken at the angular positions respectively corresponding to $q_1$ and $q_2$; marker represents 1 mm. The intensity in figure 3.a is measured through a slit parallel to the line (s).

![Graph](image1)

![Graph](image2)

![Image](image3)

![Image](image4)

The metastable state corresponding to the value $q_1$ of the wave vector (Fig. 3c; point C in Fig. 2) is the opposite, in the lateral parts of the sample, the wave vector quickly takes the new equilibrium value $q_2$ (Fig. 3d; point D in Fig. 2). This observation can be related to the crystalline quality of the sample. As a matter of fact, the 020 Bragg topograph clearly demonstrates that the central part contains a lot of dislocation lines (L, Fig. 4a) and a highly strained region (A, Fig. 4a) while the lateral parts are nearly perfect as shown by the presence of Pendelloßung fringes (F, Fig. 4a). Additional defects, due to radiation damage, arise also mainly in the central part of the sample (I, Fig. 4b).

Such a coexistence of metastable and equilibrium values has been observed for various $T_1 - T_2$ jumps, in a temperature region above the lock-in transition. However, when the jump is smaller than 1.5 °C, the modulation wave vector remains locked at the initial $q_1$ value; in that case, the energy of thermal activation would be smaller than the energy of interaction between modulation and defects. On the opposite, when the $T_1 - T_2$ jump reaches 3.5 °C, the equilibrium $q_2$ value is established quasi-instantaneously in the whole sample.

It is worth noting that, at higher temperature in the incommensurate phase (14 °C, point A in Fig. 2), no metastable state of the modulation has been observed. The modulation wave vector is rather uniform in the whole sample as shown by the satellite topograph (Fig. 4c); only the highly strained region of the sample is out of reflection (A,
Fig. 4. — Topographs of (TMA)$_2$ZnCl$_4$. a, b) 020 reflection before (a) and after (b) radiation damage ($T = 14$ °C), c) 820 reflection ($T = 14$ °C), d) 2/5 20 reflection ($T = 5$ °C). Wavelength = 0.6 Å; sample thickness = 0.7 mm; marker represents 1 mm.

Similar features are noticed in the commensurate phase (Fig. 4d, point B in Fig. 2; the loss of contrast of satellite topographs with respect to Bragg topograph can be related to the increase of the extinction length from 140 µm to about 400 µm-500 µm since a rough estimation of the structure factor has been made from the rocking curve intensities).

4. Conclusion.

Experimental observations have been made simultaneously on satellite X-ray Synchrotron topographs and rocking curves of a (TMA)$_2$ZnCl$_4$ single crystal. The influence of extrinsic defects on the modulation wave vector is found to be particularly important in a temperature range of a few degrees above the lock-in transition. The broadening of the satellite rocking curve gives evidence of a lack of long range order in the incommensurate phase. Furthermore, relaxation effects have been shown to depend strongly on the crystalline quality. Thus, lattice defects such as dislocation lines and precipitates would play a role by impeding the movement, the creation or the annihilation of discommensurations. This study clearly demonstrates the unique contribution of X-ray imaging techniques for local investigation of incommensurate phases.

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