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Elastic neutron scattering and dielectric behaviour of 4% brominated betaine calcium chloride dihydrate (BCCD)

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Abstract. We report a combined experimental study by means of elastic neutron scattering and dielectric measurements of a partially deuterated and $x = 4\%$ brominated BCCD (Betaine Calcium Chloride Dihydrate) crystal. The lowest-temperature phase is one-dimensional modulated and characterized by the coexistence of different commensurate domains (with $\delta = 1/4$, 4/17, 2/9 and 1/5 on cooling), but with a clear predominance of the five-fold phase. A huge global thermal hysteresis of the wave-vector of the modulation, attaining values of about 9 K in the incommensurate phase and up to 15 K in the "harmless" low temperature part of the phase diagram, is observed up to T_i. The role of lattice defects on this phenomenon is discussed. Similarly to the behaviour of the pure compound, the structural modulation evolves on cooling towards a soliton regime (growth of third and fifth-order satellite peaks), probably with respect to a non-stabilized non-modulated ferroelectric phase. The critical temperatures deduced from dielectric constant and pyroelectric current measurements are in very good agreement with those obtained from neutron scattering. The dielectric anomaly observed in $\epsilon_b''(T)$ at $T \simeq 85$ K, and known as the "T_s-anomaly", could not be related with any special feature detected in the neutron data, and in particular no correlation between this anomaly and the appearance of the soliton regime can be established.

PACS. 61.12.-q Neutron diffraction and scattering – 64.70.Rh Commensurate-incommensurate transitions – 77.22.Ch Permittivity (dielectric function)

1 Introduction

Betaine Calcium Chloride Dihydrate (BCCD, or $(CH_3)_3NCH_2COOCaCl_2(H_2O)_2$) is a fascinating example of a crystal exhibiting a Devil's staircase behaviour, its phase sequence [1–5] being constituted by a wealth of commensurate and incommensurate (INC) one-dimensional modulated phases ($\mathbf{k} = \delta(T)\mathbf{c}^*$) occurring between an orthorhombic paraelectric phase (space-group Pnma, above $T_\mathrm{i} = 164$ K) [6,7] and a non-modulated ferroelectric phase (space-group Pn2_1a, below $T_0 = 46$ K) [7,8]. BCCD is made of two elementary units: a betaine radical $(CH_3)_3NCH_2COO$ and an inorganic distorted octahedron, containing a Ca^{2+} ion, two Cl^- ions, two water molecules and two oxygen atoms which are shared by the carboxyl group of the organic part. At room-temperature, the unit cell ($a = 10.95$ Å, $b = 10.15$ Å and $c = 10.82$ Å) [7] contains four formula units. In the reference structure, the Ca octahedron and the carboxyl group of the betaine form quasi one-dimensional chains directed along **a** where the organic groups are branched with its axis mainly oriented along **c**. These layers are interconnected in the (0 1 1) plane by asymmetric (Cl···H-O) H-bonds.

The structural modulation, which results from the softening above T_i of a mixed optic-acoustic mode of Λ_3 symmetry [9], can be described by the libration of the betaine molecules around an axis belonging to the mirror plane m [10,11]. This modulation originates the onset of small spontaneous electric polarizations for certain commensurate values of the modulation wave-vector ($\mathbf{P}$ // $\mathbf{b}$ if δ = even/odd, $\mathbf{P}$ // $\mathbf{a}$ if δ = odd/even and $\mathbf{P} = \mathbf{0}$ if δ = odd/odd) [1,5,12–14]. This fact accounts for the great interest of dielectric and pyroelectric measurements to the study of the phase transitions in this compound.

The partial replacement of chlorine by bromine leads to compounds exhibiting special new features. The crystals grown with bromine concentrations (x) smaller

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than 38% show, at room-temperature, the same Pnma structure as pure BCCD [15]. They are therefore referred to as brominated BCCD crystals.

As bromine has a ionic radius ($r_{Br^-} = 1.95$ Å) larger than that of chlorine ($r_{Cl^-} = 1.81$ Å), partial bromination breaks locally the molecular mirror plane m and increases the average size of the unit cell (negative chemical pressure). Thus, the balance between intra and inter-layers couplings is altered and the phase diagram is strongly modified. Indeed, dielectric measurements, Raman and infrared scattering studies have shown that (i) the phase transitions are shifted towards lower temperatures when x increases; (ii) the temperature range of stability of the commensurate phases decreases when x increases and these phases are suppressed above $x \simeq 15\%$ (but the INC phase remains up to $x \simeq 30\%$) [16]; (iii) the non-modulated ferroelectric phase is absent for $x > 2\%$ [17,18]. Furthermore, bromine atoms, which can be considered to be extrinsic lattice defects for low values of x, can pin the discommensurations. This pinning hampers the switching of electric dipoles, broadens and decreases the critical anomalies, suppress some narrow commensurate phases and contributes to the shift of the phase transitions temperatures. Recently, Schaack *et al.* have reviewed the presently available information on brominated BCCD [19].

In spite of the large amount of experimental and theoretical studies on BCCD, several questions are still open. The dielectric anomaly at T_s (corresponding to the crossing of the "strange" or "Schaack" line in the (P, T) or (T, x) phase diagrams) [16–18,20] remains to be studied from a diffraction point of view. The role of lattice defects in BCCD and their connection to the global thermal hysteresis [21] is still unknown. Finally, in the case of brominated BCCD, most of the conclusions reviewed above were established from macroscopic or indirect methods. For instance, the temperature dependence of the modulation wave-vector was inferred from dielectric measurements or spectroscopic studies. A microscopic technique is therefore needed to confirm previous results or fulfill some missing informations. Neutron scattering appears more appropriate in comparison with X-ray diffraction to study pure BCCD, but also brominated one, for at least two reasons which are connected with irradiation effects: (i) Kiat *et al.* [22] have shown that phase diagrams deduced from the later technique can correspond to "non-equilibrium" behaviour; (ii) at constant temperature, third-order satellite peaks vanish with time under X-ray irradiation [23]. The present work reports detailed elastic neutron scattering and dielectric studies of a partially deuterated and 4% brominated BCCD single-crystal. Specific attention is given to the study of thermal hysteresis, to the search of high-order satellite peaks and to the possible correlation between the elastic neutron scattering response and the "T_s-anomaly". The results obtained are compared with dielectric data in order to enlighten the mechanisms underlying the phase transitions.

2 Experimental methods

The single-crystal of partially deuterated and 4% brominated BCCD was grown by slow evaporation from a saturated D_2O solution of 10% brominated calcium chloride and betaine. The bromine concentration in the crystal was inferred from the studies reported by Le Maire [16] on the solid state solubility of the system and confirmed by the value of T_i observed experimentally by dielectric measurements. Samples cut from this crystal were used for elastic neutron scattering, dielectric and pyroelectric measurements. The sample used for neutron scattering had a volume of about 8 cm^3 and a mosaic spread of 12$'$. For dielectric and pyroelectric measurements, oriented platelets of about $5 \times 10 \times 1$ mm were cut, polished and covered with gold.

The elastic neutron scattering experiment has been carried out on the triple axis spectrometer 4F1 located on a cold source at Orphée reactor, Saclay, France. The sample was enclosed in an aluminium container which was mounted on the cold finger of a displex closed-cycle cryostat. The temperature stability was better than 0.05 K. We have used a monochromatic incident beam with $k_i = 1.55$ Å^{-1}, *i.e.*, $\lambda_i = 4.05$ Å filtered from second harmonic contamination with polycrystalline beryllium cooled at nitrogen temperature. The horizontal collimations before and after the analyzer were equal to 10$'$. In the (0 k l) scattering plane, **Q**-scans along the $\mathbf{c}^*$ reciprocal direction were performed around the (0 1 3) main reflection. This latter zone has been chosen because previous data collected in the above-defined scattering geometry have shown that a third-order satellite peak is well observed at 80 K. Note that in this specific scattering plane, only the satellite peaks belonging to the main reflections with $k+l =$ even are not forbidden by the extinction rules of the superspace-group P(Pnma):(1, s, -1) [10] and this point is confirmed by the present study. Therefore, when δ is rational, *i.e.*, in the commensurate phases of the Devil's staircase, between two main reflections along $\mathbf{c}^*$ (*e.g.*, between (0 k l) and (0 k $l+1$)), the satellite peaks are not superimposed with other peaks and can be well discriminated. A superimposition can eventually occur (depending on the value of δ) only with high-order satellite peaks belonging to a (0 k $l+2$) main reflection. Elastic cooling and heating runs were performed in the temperature range $21\,\mathrm{K} < T < 300\,\mathrm{K}$. We report results on the temperature dependence of the odd-order satellite peaks (0 1 3 $\pm$ 1), (0 1 3 3) and (0 1 3 5), even-order satellite peaks being very weak. For each selected temperature, a stabilization time of roughly 20 minutes was allowed before the **Q**-scan run. Then, the experimental profile of the collected signal was systematically fitted taking into account the experimental resolution [24]. The Full Width at Half Maximum (F.W.H.M.) of the Gaussian resolution function around the (0 1 3) Bragg peak was equal to 0.634×10^{-2} Å^{-1} and to 0.736×10^{-2} Å^{-1} for longitudinal and transverse scans, respectively.

The dielectric constant was measured along **a** and along **b** in the temperature and frequency range 20 K $< T <$ 300 K and 1 kHz $< \nu <$ 13 MHz, respectively. The

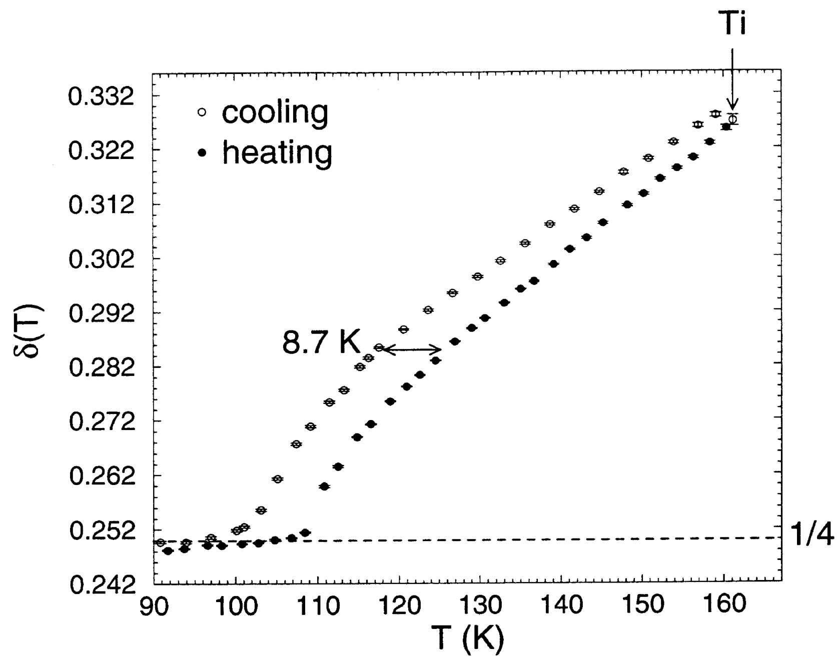

Fig. 1. Temperature dependence in the INC phase on cooling and on heating of $\delta(T) = k(T)/c^*$ deduced from the average of the positions of the satellite peaks (0 1 3 ±1). The plateau at $\delta = 1/4$ is indicated, together with the highest value of the global hysteresis.

electric field was equal to 100 mV/mm. Cooling and heating runs were performed at rates smaller than 0.5 K/min. Pyroelectric currents were measured by a short circuit technique [25] at temperature scanning rates of about 1 K/min.

3 Elastic neutron scattering measurements

3.1 Phase diagram

Figures 1 and 2 show the temperature dependence of the modulation wave-vector in the INC phase and in the low temperature commensurate phases sequence, respectively. At each temperature, the value of δ has been determined from the average of the positions of the first-order satellite peaks $(0\ 1\ 3 \pm 1)$ in Figure 1, and from the position of the third-order satellite peak (0 1 3 3) in Figure 2.

The $\delta(T)$ behaviour displayed in Figure 1 for cooling and heating runs is typical of the observed one in INC phases. Indeed, between $T_{\rm i} \simeq 161$ K and the lock-in transition at $\delta = 1/4$ ($T_{1/4} \simeq 101$ K on cooling), $\delta(T)$ decreases continuously and, like in pure BCCD [26], two regimes can clearly be discriminated. A first one down to $\simeq 115$ K, where $\delta(T)$ follows a linear evolution, and a second one between 115 K and $T_{1/4}$, where $\delta(T)$ decreases steeply. No commensurate phase, in the limit of the lowest temperature step ($\simeq 1$ K), can be detected in this INC phase. In particular, the phase 2/7, which stabilizes in the middle of the INC phase in pure BCCD (for 126.8 K $> T >$ 124 K [22]) and which separates the two regimes aforementioned, is either absent or has a range of stability smaller than 1 K.

The remarkable point is the occurrence of a huge thermal hysteresis of $\delta(T)$ in the INC phase and up to $T_{\rm i}$ (Fig. 1). This so called "global" hysteresis has an amplitude of about 9 K and has been previously observed in the pure compound [21,27], also up to $T_{\rm i}$ but with a much lower amplitude (1-3 K). Hence, it appears that the "global" hysteresis in BCCD depends on the concentration of extrinsic lattice defects, as it is on the bromine concentration: an amplification effect of the "global" hysteresis clearly occurs when the concentration of defects increases. We shall discuss the origin of this phenomenon in Section 5, in correlation with the different theories or explanations presently available for other INC compounds [28], and more specifically for thiourea [29,30].

At lower temperature (Fig. 2), the phase diagram is more complex and can be schematically described as follows: on cooling, the well-known phase 1/4 is stable over a large range of temperature ($\simeq 40$ K) up to $T_{\rm L.T.} \simeq 61$ K without any notable feature. Then, a first order transition, described step by step in temperature in Figure 3, occurs at $T_{\rm L.T.}$ towards what we shall call hereafter the "Lowest-Temperature" (L.T.) phase. Roughly, this L.T. phase is similar to the five-fold phase of the pure compound, but with two main differences which are evidenced from a careful inspection of the data, in particular those corresponding to the third-order satellite peak. Firstly, in the cooling run, the coexistence of four phases with $\delta = 1/4$, 4/17, 2/9 and 1/5 is clearly seen during the transition at $T_{\rm L.T.}$ (see the inset of Fig. 3 at 57.5 K) and does not

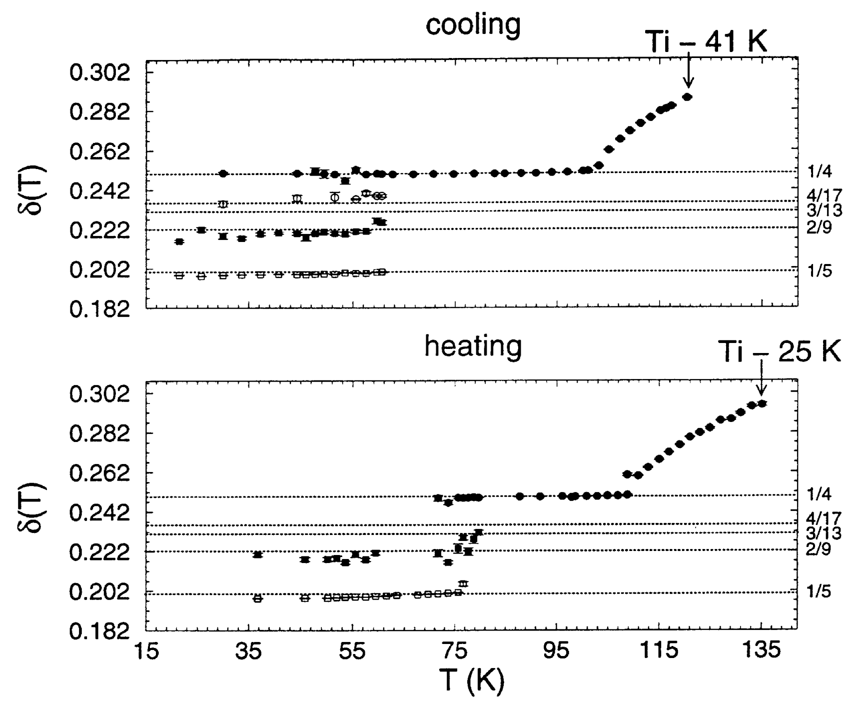

Fig. 2. Temperature dependence on cooling (top) and on heating (bottom) of $\delta(T) = k(T)/c^*$ deduced from the position of the satellite peak (0 1 3 3). The plateaus at $\delta = 1/4$, 4/17, 3/13, 2/9 and 1/5 are indicated.

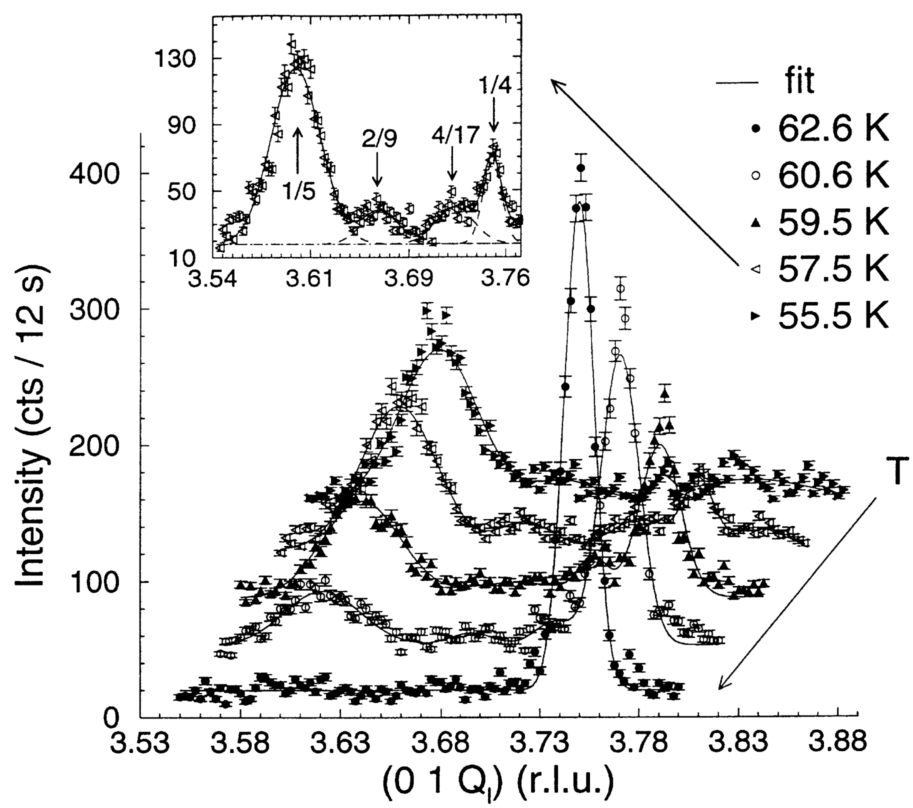

Fig. 3. **Q**-scan along $\mathbf{c}^*$ around the (0 1 3 3) satellite peak at five temperatures on cooling around the transition from the phase 1/4 towards the lowest-temperature phase. The inset shows the coexistence of four phases with $\delta = 1/4$, 4/17, 2/9 and 1/5 at $T = 57.5$ K. The peaks are fitted with a Gaussian function [24].

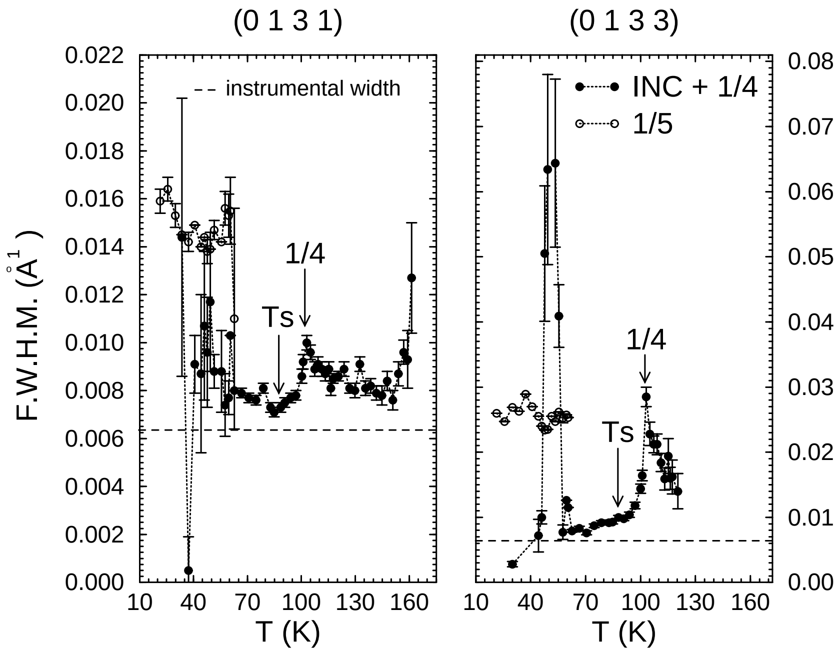

Fig. 4. Temperature dependence on cooling of the Full Width at Half Maximum (F.W.H.M.) of the (0 1 3 1) and (0 1 3 3) satellite peaks (Gaussian fit), on the left and on the right, respectively. The instrumental F.W.H.M. is indicated. Dotted lines are guides for the eyes.

completely disappear up to the lowest temperature reached (21 K). The integrated intensity of the third-order satellite peak locked at $\delta = 1/5$ is at least seven times higher than the sum of the integrated intensities of the third-order peaks locked at $\delta = 1/4$, 4/17 or 2/9. Therefore, the phase "1/5" of this doped BCCD never really stabilizes alone unlike what is observed for the pure compound [3,26,31]. Moreover, for the non-dominant $\delta = 1/4$, 4/17 and 2/9 phases in the L.T. phase, the third-order satellite peak (0 1 3 3) is obviously weak and difficult to fit. This explains why we did not report every data point of the corresponding plateaus (Fig. 2). Secondly, for the dominant $\delta = 1/5$ phase, we have observed that the first and third-order satellite reflections have widths that are respectively two and three times higher than the width (instrumental resolution) of the corresponding reflections collected in the $\delta = 1/4$ phase above $T_{\mathrm{L.T.}}$ (Fig. 4). Such an increase of the widths of the reflections can be related to the increase of structural disorder and to the stabilization of finite size domains of the $\delta = 1/5$ phase coexisting with non-dominant domains corresponding to the $\delta = 1/4, 4/17$ and 2/9 phases. From these results it is therefore clear that the phases with $\delta < 1/5$, including naturally the homogeneous non-modulated ferroelectric phase of the pure compound, do not appear in the 4% brominated BCCD.

On heating, the conclusions drawn in the previous paragraph are still valid, except in what concerns the observation of a clear plateau corresponding to $\delta = 4/17$ (bottom of Fig. 2). Such a phenomenon, *i.e.*, the non-reproducible appearance of a commensurate phase for increasing and decreasing external parameter, has been previously observed in Rb_2ZnBr_4 by Parlinski *et al.* [32], but under hydrostatic pressure. The term of "pseudo-commensurate" phase has been used in this case. In the present study, such a conclusion is limited by the weakness of the signal. Lastly, an anomalous thermal hysteresis of the wave-vector of the modulation is also observed in the "harmless" low temperature part of the Devil's staircase. For example, the transition temperature towards the L.T. phase is shifted by more than 15 K between the cooling and heating runs. This result is consistent with a strong first order character of the phase transitions in this temperature range.

3.2 Temperature evolution of the intensity of the satellite peaks

The temperature dependence of the integrated intensity of the odd-order satellite peaks around the main reflection (0 1 3), *i.e.*, (0 1 3 1), (0 1 3 3) and (0 1 3 5) reflections, is reported in Figure 5, on cooling and on heating runs. Actually, the fifth-order satellite peak (0 1 3 5) is superimposed with the non-negligible third-order one (0 1 5 −3) in the phase 1/4 but not in the phase "1/5" (or L.T. phase) where it is located at the symmetry non-allowed main reflection (0 1 4 0) position. Thus, the intensity of the fifth-order reflection (0 1 3 5) was reliably determined in the L.T. phase only, even though in this phase the (0 1 3 5) peak is, in principle, still superimposed with another fifth-order satellite peak (the (0 1 5 −5) one). However, this peak is probably almost extinct, since no significant decrease of the intensity of the third-order satellite peak (0 1 3 3) occurs at $T_{\mathrm{L.T.}}$ (see Fig. 5), when the two reflections (0 1 5 −5) and (0 1 3 3) are no longer superimposed

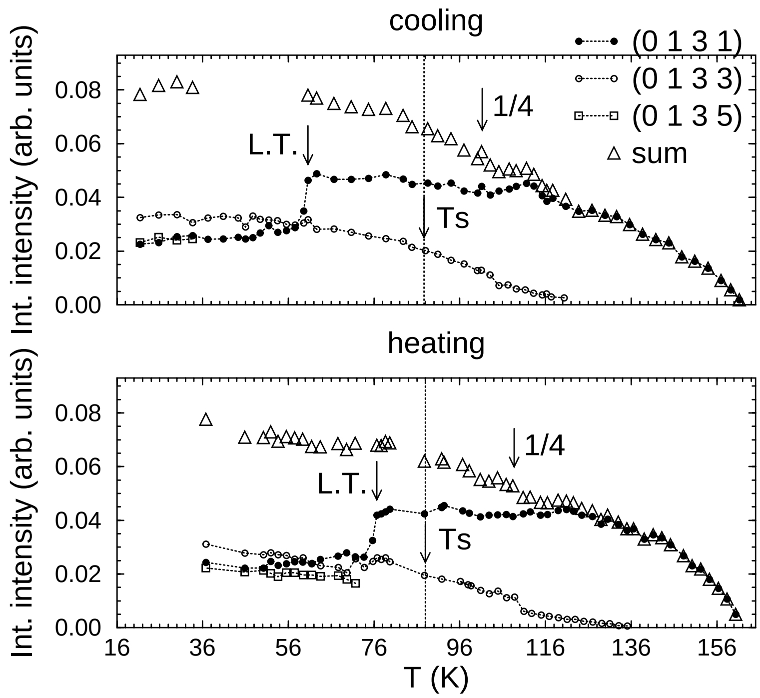

Fig. 5. Temperature dependence of the integrated intensity of the odd-order satellite peaks around the Brillouin zone (0 1 3) on cooling (top) and on heating (bottom). In the case of phase coexistences, the different contributions have been added. The fifth-order satellite peak (0 1 3 5) can be discriminated from first and third-order satellite peaks only in the lowest-temperature (L.T.) phase (or phase "1/5"). The triangles up "sum" correspond to the sum of the intensities of the (0 1 3 1), (0 1 3 3) and (0 1 3 5) peaks; when the peak (0 1 3 5) has not been measured, those points are omitted. Dotted lines are guides for the eyes.

due to change of the modulation periodicity (see Sect. 2). As already stressed, the even-order satellite peaks, *i.e.*, second or fourth-order ones, are negligible. Below $T_{\mathrm{L.T.}}$, in the phase-coexistence regime, we have chosen to sum the integrated intensity of the different satellite peaks corresponding to the same order. Lastly, all the fits have been done taking into account the spectrometer resolution and assuming for the diffraction peaks a Gaussian shape [24].

In the INC phase, the temperature evolution of the integrated intensity of the first-order satellite peak ($I_1(T)$) is very similar to the one in the pure compound [26,31]. The critical exponent β, associated to the primary order parameter in the vicinity of T_{i}, can be deduced from the curve $I_1(T)$, insofar as $I_1(T)$ is proportional to the squared order parameter, *i.e.*, $I_1(T) \propto (T_{\mathrm{i}} - T)^{2\beta}$. The best linear fitting of $\log_{\mathrm{e}}(I_1(T))$ *versus* $\log_{\mathrm{e}}((T - T_{\mathrm{i}})/T_{\mathrm{i}})$ on cooling and on heating in the temperature range 161 K–127 K and 141 K–160 K, respectively (thus in the harmonic regime only), obtained for the value $T_{\mathrm{i}} = 161.63$ K, gives a value of $\beta = 0.33(1)$ and $0.34(1)$, respectively (Fig. 6). Hence β has the same value both on heating and on cooling runs. This value is in fact in very good agreement with the one found in the pure system by means of quadrupolar perturbed NMR [33], *i.e.*, $\beta = 0.345$, even though our temperature step used during the data collection in this range of temperature ($\simeq 2$ K) is far too large for a precise determination of a critical index near T_{i}. Moreover, the values of β and of T_{i} appear very sensitive to the number

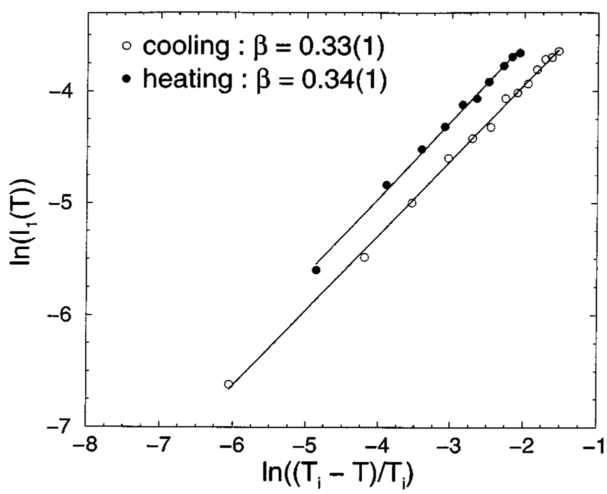

Fig. 6. The natural logarithm of the integrated intensity of the first-order satellite peak (0 1 3 1), $\ln(I_1(T))$, *versus* $\ln((T_{\mathrm{i}} - T)/T_{\mathrm{i}})$, in the vicinity of $T_{\mathrm{i}} = 161.63$ K, on cooling and on heating. For both evolution, the linear curve fitting is drawn and the critical exponent so deduced is indicated. E.s.d.'s are given in parenthesis.

of points (or the temperature range) considered during the fit procedure.

As observed in pure BCCD [21], third-order satellite reflections appear in the INC phase, more roughly around $T_{\mathrm{i}} - 40$ K (Fig. 5). Then, on cooling, the integrated

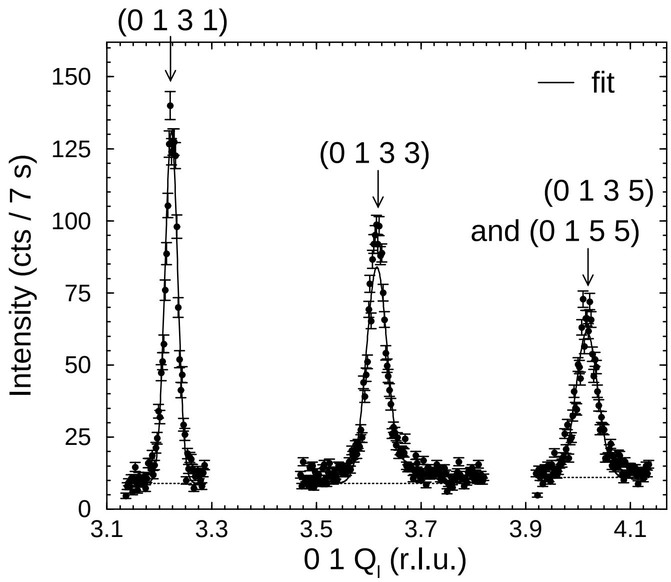

Fig. 7. **Q**-scan along $\mathbf{c}^*$ around the (0 1 3) Brillouin zone showing the strong intensity of odd-order satellite peaks (third and fifth-order ones) in the lowest-temperature phase (or phase "1/5") at 30 K. The fifth-order satellite peaks (0 1 3 5) and (0 1 5 −5) are superimposed in this phase. The peaks are fitted with a Gaussian function [24].

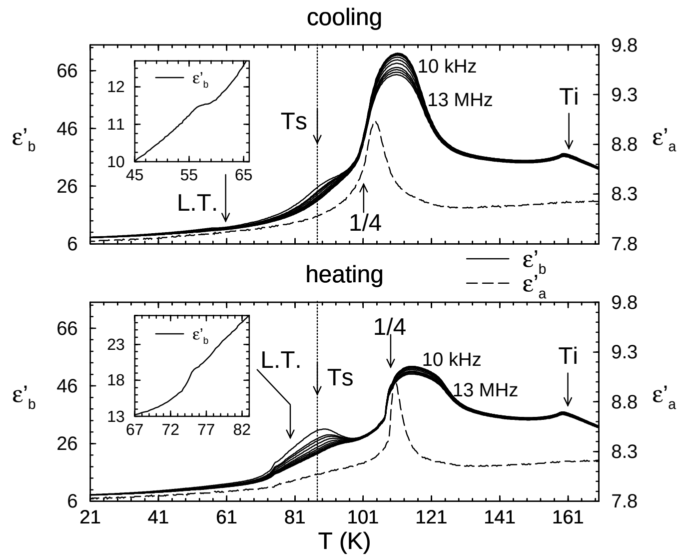

Fig. 8. Temperature dependence of the real part of the dielectric constant along **a** ($\epsilon'_a(T)$) and along **b** ($\epsilon'_b(T)$) on cooling (top) and on heating (bottom). $\nu = 100$ kHz for $\epsilon'_a(T)$ and for the two insets of $\epsilon'_b(T)$; $\nu = 10$ kHz, 60 kHz, 100 kHz, 600 kHz, 1 MHz, 2 MHz, 4 MHz, 6 MHz, 8 MHz, 10 MHz, 11 MHz, 12 MHz and 13 MHz for $\epsilon'_b(T)$. The transition towards the lowest-temperature (L.T.) phase is indicated.

intensity of these peaks increases rapidly and monotonously up to the lowest temperature reached, thus indicating that the modulation becomes strongly anharmonic below $T_{1/4}$. Moreover, the possibility to discriminate large "pure" fifth-order satellite reflection in the L.T. phase (Fig. 7), indicates clearly that the structural modulation becomes strongly anharmonic at low temperature. This structural anharmonicity can be qualitatively explained by the strong contribution to the global static distortion of the odd-order harmonics, namely third and fifth-order ones. Then, presumably, the modulation has the same squared shape already evidenced in the pure compound [23,34], even though only a complete structural study would give the quantitative features of the atomic modulations. Following what has been studied in the pure compound [23,34], we may assume that below $\simeq T_{1/4}$, the modulated structure is made of ferroelectric domains separated by walls, or discommensurations, where the phase of the modulation follows a two-steps sine-Gordon law, typical of a soliton regime with respect to a non-modulated ferroelectric phase [35,36], although this last phase is not stabilized in the compound under investigation.

Finally, let us return to the temperature dependence of the integrated intensity of the satellite reflections (Fig. 5). Like in the pure compound [21,26,31], the intensity of the first-order satellite peaks $I_1(T)$ increases on cooling from $T_\mathrm{i} = 162$ K down to $T \approx 80$ K and then saturates below this temperature (58 K $\leq T \leq$ 80 K). However, at the onset of the L.T. phase, $I_1(T)$ abruptly decreases to lower values and remains nearly constant in all the range of stability of this phase. Note also that in this L.T. phase, the fifth-order satellites can be discriminated and registered (see also Fig. 7).

If the contribution of the fifth-order satellite peaks is assumed to be negligible in all the temperature range of stability of the four-fold phase, the unusual behaviour of $I_1(T)$ can be interpreted as due to the abrupt rise of the fifth-order satellite reflections. The total diffraction intensity would be conserved and the solitonic structure of the modulation would be strongly increased in the L.T. phase. In this case, the temperature dependence of the sum of the integrated intensities of the first, third and fifth-order satellite peaks, would indicate that a monotonous temperature dependence of a pseudo-order parameter could be recovered for all the phase sequence, even in the L.T. phase (triangles up of Fig. 5), with a pseudo-critical exponent equal to 0.5. On the other hand, if the fifth-order satellite peaks (although not detectable for the reasons explained above) are already present in the four-fold phase, then the total diffraction intensity would not be conserved and the amplitude of the modulation wave would also be effectively reduced at the entrance of the L.T. phase. This possible decreasing of the amplitude of the modulation could be due to an increase of the elastic energy associated with the onset of different domains in this disordered phase. In any case, the observed effect is reversible since, in the heating run (bottom of Fig. 5), one observes that $I_1(T)$ rapidly increases when the system enters the $\delta = 1/4$ phase and recovers the same initial value in the INC phase.

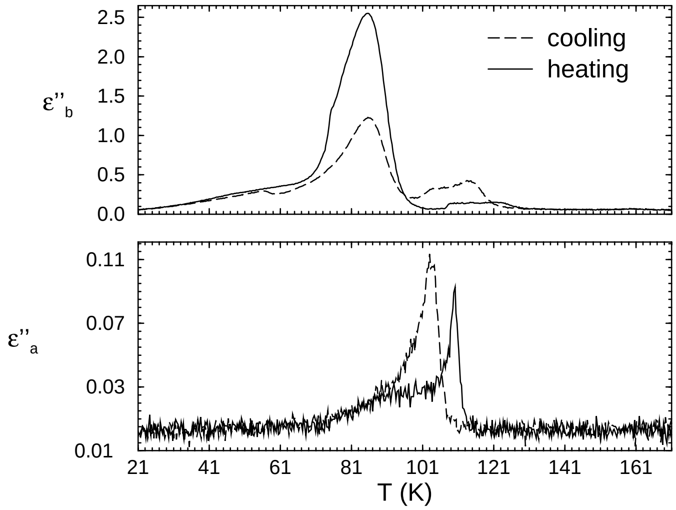

Fig. 9. Temperature dependence of the imaginary part of the dielectric constant along **b** ($\epsilon_b''(T)$) (top) and along **a** ($\epsilon_a''(T)$) (bottom) on cooling and on heating at $\nu = 100$ kHz.

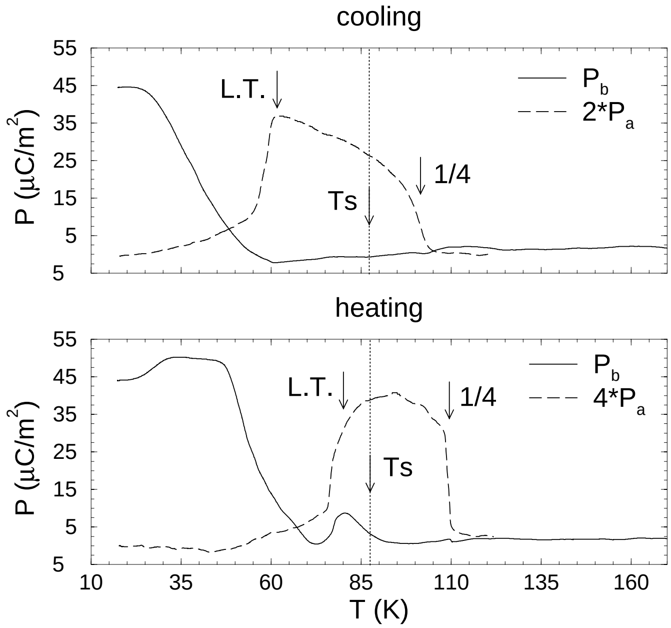

Fig. 10. Temperature dependence of the electric polarizations along **a** ($P_a(T)$) and along **b** ($P_b(T)$) on cooling (top) and on heating (bottom), obtained from the measurement of the pyroelectric current under a d.c. field of 6.4 V/cm along **a** and of 100 V/cm along **b**. The transition towards the lowest-temperature (L.T.) phase is indicated.

4 Dielectric measurements

4.1 Dielectric constant

The temperature dependence of the real part of the dielectric constant along **a** and along **b**, *i.e.*, $\epsilon_a'(T)$ and $\epsilon_b'(T)$, respectively, is shown in Figure 8 on cooling and on heating, together with the frequency dispersion of $\epsilon_b'(T)$. As can be seen, the anomalies detected are well correlated with the transitions observed by elastic neutron scattering. The two small anomalies in $\epsilon_b'(T)$ observed at $T \simeq 160$ K and at $T \simeq 58$ K on cooling (see inset of Fig. 8) mark the transition from the paraelectric towards the INC phase (at $T_{\rm i}$) and from the phase 1/4 towards the L.T. phase, respectively. Two more prominent anomalies in $\epsilon_b'(T)$ are seen around $T \simeq 120$ K and around $T_{\rm s} \simeq 85$ K. The first of these anomalies is clearly related to the presence of detectable third-order satellite peaks. Its origin is therefore linked to the rise of discommensurations, polar along **b**, associated to the progressive onset of a non-sinusoidal (solitonic) modulation. The second of these anomalies, at $T_{\rm s} \simeq 85$ K, which is better seen in the temperature dependence of the imaginary part of the dielectric constant along **b**, *i.e.*, $\epsilon_b''(T)$ (Fig. 9), has been previously reported as the "$T_{\rm s}$-anomaly" by several authors [16–18, 20] for different Br concentrations. Its origin is presently matter of debate. We will return to this point in Section 5. Note that this anomaly occurs in the middle of the phase 1/4 for $x = 4\%$, therefore without changing of the modulation periodicity, and cannot be clearly related with any anomaly in the temperature dependence of the intensity of the first or third-order satellite peaks (see Fig. 5). In particular, at $T_{\rm s}$, the modulation is already clearly anharmonic. Finally, the unique anomaly detected both in ϵ_a' (Fig. 8) and in ϵ_a'' (Fig. 9) corresponds to the transition towards the four-fold phase.

The phase sequence measured in the heating run (bottom of Fig. 8) reveals globally quite similar features. The different behaviour of the dielectric constant ϵ_b' observed on heating and on cooling may indicate that different patterns of discommensurations are effectively stabilized in the 1/4 and INC phases on heating and on cooling. At the continuous (second order) transition between the Pnma and the INC phase such effects are obviously absent and no thermal hysteresis is found within the experimental error. It should be stressed that the prominent "$T_{\rm s}$-anomaly" in $\epsilon_b''(T)$ at $T_{\rm s} \simeq 85$ K does not display any relevant temperature hysteresis (Fig. 9).

A relaxation due to a freezing of the soliton lattice in a disordered system with non-uniform distributions of valleys and potential barriers due to bromination, would imply a noticeable dielectric dispersion as it is experimentally found. Figure 8 shows $\epsilon_b'(T)$ measured at different frequencies in the range 10 kHz-13 MHz. Dielectric dispersion in this frequency range is observed in the INC phase near the lock-in transitions at $\delta = 1/4$ and around $T_{\rm s}$. However, while this dispersion phenomenon in the INC phase near $T_{1/4}$ is accompanied by a slight anomaly in the F.W.H.M. of the first and third-order satellite peaks (Fig. 4), no such clear anomaly is found around $T_{\rm s}$. This anomaly discloses an increase of the structural disorder accompanying the rise of discommensurations in the INC phase.

4.2 Pyroelectric current

The temperature dependence of the electric polarizations along **a** ($P_a(T)$) and along **b** ($P_b(T)$), obtained from the measurement of the pyroelectric current under a d.c. field of 6.4 V/cm along **a** and of 100 V/cm along **b**, is displayed in Figure 10 on cooling (top) and on heating (bottom). The agreement of these polarization data with the phase sequence observed by neutron scattering is excellent. Along the **b** direction and in the cooling run, a small polarization P_b of about 45 μC/m^2 is observed below $T_{\rm L.T.}$. This polarization likely results from the stabilization of commensurate polar domains with wave-vectors 4/17 and 2/9, corroborating the fact that the L.T. phase results from the coexistence of at least the **b** polar commensurate phases 4/17 and 2/9. Nevertheless, this kind of measurement does not allow to discriminate between these two last phases, polar along the same direction. In the heating run, in addition to this polarization which is shifted in temperature, appears a small peak around $T \simeq 80$ K, corresponding to a very tiny polarization of the order of $5\,\mu$C/m^2. However, as a similar anomaly is not detected in the decreasing run at this temperature, we can not unambiguously ascribe its origin to the process responsible to the dielectric anomaly at $T_{\rm s} \simeq 85$ K. The electric polarization measured along **a** does not reveal any detectable anomaly in the vicinity of $T_{\rm s}$, but indicates clearly the temperature range of existence of the phase 1/4. Note that the temperature dependences of the polarization observed in the cooling and in the heating runs are rather different.

5 Conclusions

The present combined experimental study of partially deuterated and 4% brominated BCCD, by means of elastic neutron scattering, dielectric and pyroelectric measurements, has mainly shown that (i) the lowest-temperature phase, or L.T. phase, is one-dimensional modulated and results from the coexistence of commensurate domains with $\delta = 1/4$, 4/17, 2/9 and 1/5 on cooling (on heating, the phase 4/17 can not be confirmed) with a clear predominance of the five-fold phase; (ii) the "global" thermal hysteresis of the wave-vector of the modulation in the INC phase is dramatically increased by the presence of extrinsic lattice defects, in comparison with its amplitude in the non-doped compound [4,21,37]; (iii) a soliton regime, probably with respect to a non-stabilized non-modulated ferroelectric phase, develops on cooling, as in the pure compound [23,34]; (iv) the "$T_{\rm s}$-anomaly" [16,17,20], confirmed and characterized from a dielectric point of view, can not be related with any special feature detected in the neutron data, in particular no correlation with the appearance of the soliton regime aforementioned can be established. Let us now discuss the points (ii) and (iv).

Firstly, the so-called "global" hysteresis has been studied many times in the past [28], but it seems that a complete and quantitative explanation is not yet available. Indeed, two main problems remain, which are related to the fact that in BCCD, but also in thiourea [30], this hysteresis persists up to $T_{\rm i}$. On the one hand, in the intrinsic theory [38], the appearance of the "global" hysteresis correspond to a breaking of ergodicity, which is not expected to occur at or almost at $T_{\rm i}$. On the other hand, in the extrinsic theory [39], a pre-requisite is often the presence of domain walls or discommensurations, but in pure or doped BCCD the modulation is unambiguously harmonic near $T_{\rm i}$. Nevertheless, Lederer *et al.* [29] have shown in thiourea that even a sinusoidal modulation exhibits hysteresis, generated by the pinning force due to "frozen-in" extrinsic defects. The present study confirms the fact that the "global" hysteresis is enhanced by the introduction of extrinsic lattice defects. As a conclusion, one can say that it's probably impossible, due to the irreducible presence of defects in real systems, to discard the theoretical intrinsic contribution to this hysteresis phenomenon, even if its contribution near $T_{\rm i}$ seems not to be relevant.

Secondly, the physical origin of the dielectric anomaly at $T_{\rm s}$ remains not clear. Presently, two interpretations can be found in the literature. Le Maire *et al.* [16,17,20] have suggested that this anomaly could be due to a freezing of the soliton lattice, *i.e.*, $T_{\rm s}$ would mark the onset of collective shifts or depinning of the solitons with respect to the underlying lattice. Furthermore, in this interpretation, the modulation would be nearly sinusoidal above and strongly anharmonic below $T_{\rm s}$. Clearly, our results cannot support this explanation. A second origin for the "$T_{\rm s}$-anomaly" was proposed in a recent paper by Neubert *et al.* [40]. According to these authors and on the grounds of a numerical analysis of a Double Ising Spins model for one-dimensional displacively modulated materials, the "$T_{\rm s}$-anomaly" could mark an internal first order phase transition between phases with the same wave-vector but different pseudo-spins configurations. In the particular case of the four-fold phase of BCCD, this internal transition would result from the flip of four pseudo-spins of the s-type, describing the cosine or B_{3g} component of the modulation wave [23,34,40]. As a consequence, the higher order harmonics (the third-order harmonics were specifically considered in the analysis) of this cosine component of the structural distortion would be strongly increased (at the cost of the first-order harmonic) at this internal transition. In this tempting interpretation, the modulation must be already anharmonic above $T_{\rm s}$, in agreement with the present experimental study and in opposition with Le Maire *et al.*'s point of view. However, at variance with our data, the intensity of third-order satellite peaks would display a critical behaviour at $T_{\rm s}$. Hence, our results do not support this interpretation. Nevertheless, we stress that we have studied only the temperature dependence of the reflections belonging to a particular Brillouin zone and that a full structural determination of the four-fold phase, both above and below $T_{\rm s}$, would be required in order to full invalidate or confirm the ascribed origin to the "strange anomaly".

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